

Hydrogenation of German bituminous coal for distillates
by I. Romey, F. Friedrich, B. Strobel

More than fifty years ago already, conversion of coal to oils, motor fuels, and chemical feedstocks was available in Germany on industrial scale. The first hydrogenation plant was commissioned in Leuna in 1927. This plant employed the sump-phase and gas-phase hydrogenation processes developed by Bergius and Pier. At the same time the Pott Broche process for production of coal extracts and the Fischer-Tropsch synthesis for production of motor spirit and chemical feedstock were under development in Germany. After World War II, no attempt was made to reactivate the coal liquefaction technology, primarily because of economical reasons. Only since the oil crisis in 1973 further development was done on sump-phase hydrogenation for production of distillate oils from coal. The present activities are shown on table 1.

Compared to the earlier German hydrogenation process the new developments are featured particularly by the following conditions:

- Removal of solids and residual oils from the hydrogenation process by distillation rather than by mechanical separation.
- Recycling of only distillate oil for coal slurry preparation which means reduction of asphaltene concentration in the hydrogenation reaction.
- Use of the distillation residue for production of hydrogen in a downstream gasification plant.

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COMPANY	SITE (DISTRICT)	CAPACITY (COAL T/D)	BUDGET MM \$	SPONSOR	TIME SCHEDULE											
					74 75 76 77 78 79 80 81 82 83 84											
Bergbau- Forschung	Essen (Ruhr)	.5	16	State Gvt. NW (MWMV)	plant running											
Ruhrkohle Veba Oel	Bohrup (Ruhr)	200	150													
Saarberg	Reden (Saar)	.5	4	Federal Gvt. (BMFT) and State Gvt. Saar												
	Völklingen (Saar)	6	28													
Rheinbraun	Wesseling (Rhein)	.25	3	Federal Gvt. (BMFT)												

Tab. 1: Current coal hydrogenation projects in Germany

By these modifications the following improvements can be achieved:

- Lowering of the process pressure down to 300 bar
- Increase of the specific reactor throughput
- Minimize the residue problems by only producing an easily disposable mineral slag.
- Substantially increase thermal efficiency and, thus, process economics.

The Experimental Plant

In an experimental plant of Bergbau-Forschung, Essen, work is done since 1976 on the modified hydrogenation process. Work meanwhile exceeds 100 test runs totalling more than 20 000 hours of operation under hydrogenation conditions. Typical run conditions for a German bituminous coal are shown on table 2.

EXPERIMENTAL PLANT OPERATION

Reactor temperature	°C	475
Preheater outlet temp.	°C	420
Make-up hydrogen	m ³ /kg maf coal	1.00
H ₂ -Partial pressure at preheater inlet	bar	250
Total pressure	bar	300
Coal throughput	kg/l hr	.5 to .75
Type of recycle oil	middle a. heavy distillate	
Solids concn. in slurry	%	> 40
Coal particle size	mm	< .1

Tab. 2: Typical run conditions for a German coal.

Fig. 1 shows a simplified flow scheme of the experimental plant.

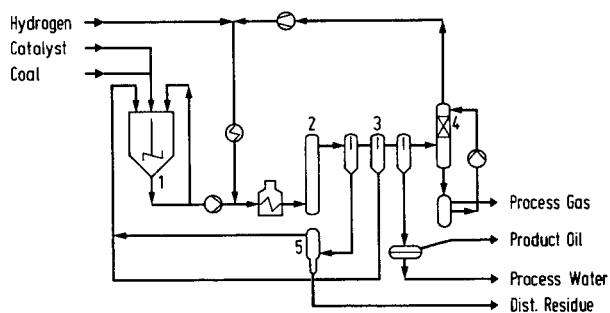


Fig. 1: BERGBAU-FORSCHUNG EXPERIMENTAL PLANT
 1 Slurry Preparation 2 Conversion 3 Separation
 4 Recycle Gas Scrubbing 5 Vacuum Flash

A pumpable slurry is made up by ground coal, recycled distillate oil, and catalyst. The slurry is fed to the hydrogenation reactor via a pre-heater. Upstream the pre-heater high-pressure hydrogen is added. After leaving the reactor the hydrogenation products are led to a series of three high-pressure separators. From the first vessel high- and non-boiling oils are drawn off together with all the solids viz some unconverted coal, mineral matter, and catalyst. The liquid is treated in a vacuum flash unit to yield a distillate oil containing no solids. Mostly middle oil is obtained from the second separator and also used for slurry preparation. In the third separator the net product oil is recovered. It consists of only light oil and middle oil. The gases that also form under reaction conditions are for the most part hydrocarbons. They are removed from the recycle gas by high-pressure oil scrubbing.

All the oils and gases produced in the hydrogenation step need upgrading to give saleable products.

Typical oil yield C₅+ from German bituminous coal is around 50 % w/w, as was shown in BF experimental-plant runs under conditions listed in table 2.

Product Oil

The distillate oil accounts for the largest portion of the product slate, i.e. for 50 % relative to the maf feed coal. The boiling point of the product oil, on average, ranges between 50 and 320°C, 30 % of the oil being in the boiling range below 200°C. Oil boiling above 320°C is not produced as net product with the new German coal hydrogenation process. It is all recycled and therefore out of the net balance.

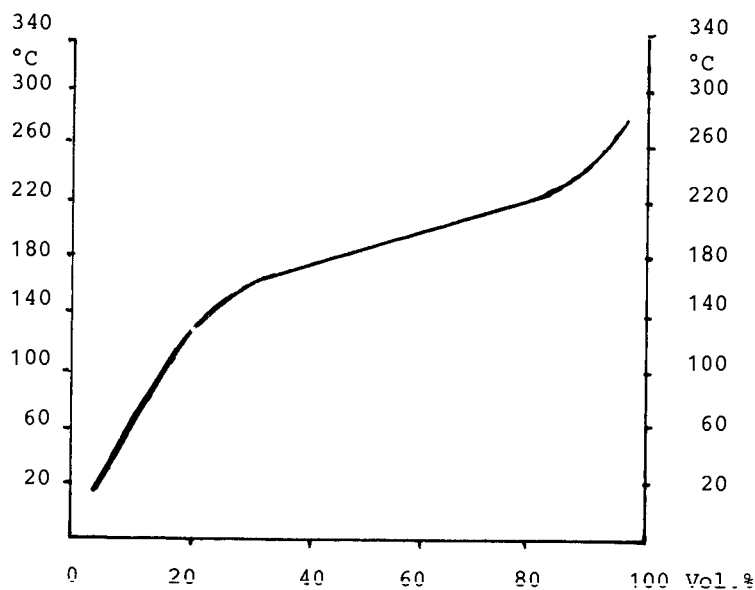
So far no detailed breakdown of all the components contained in the coal oil can be given. Sure we do know roughly the oil composition in terms of group type analyses, and there is no doubt on what individual structures the mixture is basically composed of.

However because of its origin the oil contains countless isomer compounds not only with regard to the carbon skeletons but also to the different partially hydrogenated aromatics. The product slate is further complicated due to the presence of phenol and its homologous compounds and to the presence of various nitrogen containing compounds. So only few individual compounds as phenol, all of the cresols, toluene, naphthalene, and tetrahydronaphthalene account for more than 1 % of the total oil quantity. A lot of compounds, however,

account for less than 0.1 per cent.
Some data on the properties and analytical composition of the light and medium boiling oil fraction, respectively, is listed below.

		Light Oil	Middle Oil
boiling range	°C	C ₅ - 200	200 ~ 325
density/15°C	g cm ⁻³	0.865	0.990
heating value	kJ kg ⁻¹	41 000	38 500
elemental analysis			
C	p.ct.,w/w	85.3	87.4
H	"	11.1	9.1
O	"	3.5	3.0
N	"	0.24	0.60
S	"	0.1	0.1
group type analysis			
neutral oil	p.ct.,w/w	84.35	77.3
phenols		15.4	16.2
bases		0.25	6.5

Figure 2 shows the boiling diagram of a typical product oil.



Residue

In the new German process all the remaining solids from the liquefaction step are kept in the flash distillation residue as is done also in some U.S. processes. In addition to the solids the residue contains the so-called asphaltoles, asphaltenes, as well as some heavy oil.

At elevated temperatures the organic matter forms a melt that keeps the solids suspended. Thus the residue represents a pumpable liquid that may easily be transferred to a pressurized gasifier. There by partial oxidation the hydrogen required for the liquefaction stage can be produced. Residue gasification is part of the overall process design but so far has not been investigated experimentally.

Approximately 25 p.ct. of the organic matter of the feed coal is bound in the flash distillation residue. The table gives information on the average analysis of such a residue.

Flash Distillation Residue Analysis

softening point	°C	180
volatile matter	p.ct.,w/w	30
ash content	"	26
pyridine insolubles	"	52
asphaltoles	"	9
asphaltenes	"	21
heavy oil	"	18

Hydrocarbon Gases

In bituminous coal hydrogenation gas formation mainly consists of hydrocarbons. In the plant there are several different process gases having different composition. The question whether these streams either should be combined or treated separately can only be discussed in commercial scale design. In the experimental plant the different streams are only measured and analyzed. From the analytical results we compute the overall hydrocarbon gas production based on the feed coal. This information is listed in the following table:

Hydrocarbon Gases

		saturates	olefins
methane	p.ct. w/w maf. coal	6.8	
ethane	"	5.7	
ethene	"		0.1
propane	"	5.6	
propene	"		0.3
n-butane	"	2.8	
i-butane	"	0.7	
butenes	"		0.2
total		21.6	0.6
		22.2	

In coal liquefaction the hydrocarbon gases are regarded as unavailable by-products. Nonetheless, at least the C₂ through C₄ hydrocarbons can be commercialized as valuable chemical feedstocks or fuel gases.

Water and Inorganic Gases

The inorganic compounds water, hydrogen sulfide, and ammonia as well as carbon monoxide and carbon dioxide are basically formed as by-products of coal hydrogenation. The quantities produced depend on the heteroatoms content (oxygen, nitrogen, sulfur) of the feed coal. These heteroatoms are partly converted to form hydrogen compounds.

The oxygen contained in coal is partly removed during hydrogenation as carbon monoxide and dioxide, the monoxide presumably being formed from dioxide by reduction with hydrogen. The carbon dioxide originates via decarboxylation from carboxylic groups present in the coal.

The denitrification and desulfurization reactions taking place along with the degradation of the coal is to be considered an advantage. While upgrading coal oil the heteroatoms left have to be removed anyway. On the other hand, the formation of some water from oxygen in coal may be taken as a drawback because of the consumption of hydrogen and the removal of potentially valuable phenols.

The product water is let down from high pressure together with the net product oil, and the two layers formed are subsequently separated. Dissolved in the water there are some phenols and inorganic compounds. Carbon monoxide has only poor solubility in the liquids

so it has to be removed from the high pressure gas by continuous release of some recycle gas. Carbon dioxide, ammonia, and hydrogen sulfide however dissolve sufficiently in water to be easily scrubbed from the high pressure gas by injecting some additional water. Consequently inorganic salts such as ammonium carbonate and sulfides are also present. Refining the process waste water will accordingly need much effort in commercial scale liquefaction.

Hydrogen Consumption

Hydrogen consumption on maf feed coal is 6.5 to 7.5 per cent computed on the maf feed coal, as measured in the BF experiments under the conditions listed in table 2. The consumption values cover both the chemically reacted hydrogen and the unavoidable losses. These have been determined to be about 15 % on the total hydrogen consumption. In result, the hydrogen consumed in reaction amounts to 5.5 to 6.5 per cent on maf coal.

When reducing hydrogenation severity and thus the yields - only 40 % instead of 50 % for oil, and 13 % instead of 23 % for gas - correspondingly the chemical hydrogen consumption is reduced to 4 %.

Because of the many different ways the hydrogen reacts with coal and the intermediate products, it is difficult to determine what amount of hydrogen is actually consumed with each of it. Methane for instance maybe formed from primary, secondary, and tertiary carbon atoms initially bound in coal. Each way implies a different hydrogen requirement.

Status of Development

The data and experiences from the BF experiments have been used to support design and engineering work on a 200 t/d pilot plant. The process flow sheet is essentially identical to the one of the experimental unit. Presently this demonstration project is under construction near Bottrop/Essen, Germany. The plant will be operational in mid - 1981. The program is under the responsibility of Ruhrkohle AG and Veba Oel AG, and the State Government of Northrhine-Westfalia gives major financial support.

INTERACTIONS BETWEEN SOLVENT COMPONENTS, MOLECULAR HYDROGEN AND MINERAL MATTER DURING COAL LIQUEFACTION

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INTRODUCTION

In direct coal liquefaction, the principal objective is to stabilize the molecular fragments generated by the thermal degradation of coal. Preferably, this is achieved by capping the coal-derived free radicals with hydrogen. In turn, this requires that hydrogen is provided at a rate and in a form compatible with the demand established by the thermal reaction of the coal.

Although the ultimate source of hydrogen is hydrogen gas, the most effective route for hydrogen transfer is by way of the liquefaction solvent. Hydrogen is supplied most readily from hydrogen donor compounds which generally are replenished by catalytic reactions (either externally or internally). In the absence of an adequate concentration of active donors, free radicals can be stabilized by other reactions between solvent components and coal (1).

Extensive studies have been carried out in this laboratory to examine the mechanisms of coal liquefaction in both donor and non-donor solvents. The ultimate aims of this research are to provide means of identifying and controlling the optimal recycle solvent composition in a given process.

In earlier reported work (2) certain polycondensed aromatics were identified as effective non-donor coal solvents. These compounds react with molecular hydrogen during coal liquefaction forming low concentrations of active donors, in situ. The process can be catalyzed by coal mineral matter components. In addition, it is considered that the ability of these components to effectively disperse the coal liquefaction products also contributes to their efficacy.

It is recognized that the study of single model compounds, while affording useful information, does not take into consideration the more complex situation in a real solvent where solvent-solvent interactions undoubtedly occur (1). As a first approach to this problem, the previous studies have been extended to investigate coal conversion in a binary solvent system consisting of a conventional donor (tetralin) and polycondensed aromatics. The results of these investigations are presented below.

EXPERIMENTAL PROCEDURE

Experiments were conducted with bituminous (Monterey) and sub-bituminous (Belle Ayr) coals. The coals were prepared from 1-2" diameter lumps which had been stored under an argon atmosphere (without drying) in a refrigerated room since sampled from the mine. The lumps were crushed and sieved to minus 100 mesh in a glove bag under flowing argon. When sufficient sample had been ground, it was thoroughly mixed and then sealed in small vials, still under argon. A different vial was used for each experiment, the required quantity of coal being weighed from a newly opened vial and the remainder discarded. Analyses of the prepared coals are shown in Table 1.

The conversions were carried out in a small stirred autoclave which has been described in detail elsewhere (1). Essentially this is a reactor of about 12 cc. capacity heated by a close fitting electric furnace. Agitation is provided through the movement of an oscillating plunger which is driven by an electromagnet. A relatively large free volume above the reactor is

kept cold which acts as a gas reservoir allowing operation under virtually isobaric conditions.

The reactor was loaded with a mixture of solvent and coal in the ratio of 3:1 on a dry coal basis. After pressurizing the reactor, the system was heated to the desired temperature with agitation. The time required to reach reaction temperature was an additional 30 minutes. Reproducibility of temperature profiles was good as were the calculated conversions. Several sets of repeated experiments showed a variation of less than $\pm 3\%$ in conversion.

At the end of the reaction, a quantity of tetrahydrofuran (THF) was injected into the reactor while still under pressure following which it was quenched using an ice/water bath. The objective of injecting THF was to facilitate the removal of the solid reaction products (e.g. when pyrene was the solvent) from the reactor.

After venting, the reactor contents were removed in more THF and transferred to a Soxhlet extraction thimble where they were continuously extracted in THF for 18-24 hrs under argon. Conversions were calculated on the basis of the insoluble residue.

The soluble products were analyzed by gas chromatography and GC/MS.

RESULTS AND DISCUSSION

Experiments were carried out to investigate the dissolution of Belle Ayr and Monterey coals in mixtures of pyrene with tetralin and 2-methylnaphthalene with tetralin. The effects of donor concentration, gas atmosphere and hydrogen pressure on coal conversion and hydrogen transfer from tetralin were determined. In addition, some experiments were conducted to examine the reactions between pyrene, tetralin and hydrogen gas.

Coal Conversions

Conversion to THF soluble products and gases is shown as a function of tetralin concentration for Belle Ayr and Monterey coals in Figures 1 and 2 respectively. The reactions were carried out at 400°C for 1 hr under 1000 psig gas pressure. On the two figures, data are presented showing conversions in pyrene-tetralin mixtures both in argon and in hydrogen and, for comparison, in 2-methylnaphthalene-tetralin mixtures in the presence of hydrogen.

For both coals, the conversion in the absence of a donor was enhanced by the presence of gaseous hydrogen. As has been shown (2), the conversion obtained in pyrene is higher than in a less condensed compound such as 2-methylnaphthalene and its effectiveness as a solvent is related to the formation of dihydropyrene during liquefaction.

With reference to Figure 1, the effect of adding tetralin up to about 8 wt% appeared to have little effect on conversion in the three systems shown. Further increase in the donor concentration was accompanied by increasing conversion which reached a limiting value of about 85% at tetralin concentrations of about 70% and above. At the high donor levels, the conversion was not

apparently affected by the nature of the other component or by the gas atmosphere. The major differences between the solvent systems are evident at tetralin concentrations between 8-70%.

From the Figure it is apparent that hydrogen gas is beneficial. However, at a given tetralin level methylnaphthalene based solvents with hydrogen show only a modest improvement over pyrene based solvents without hydrogen. In marked contrast pyrene based solvents respond dramatically to hydrogen pressure and at only 30% tetralin, the blended solvent is almost as effective as 100% tetralin.

The same general effects are observed for the conversion of Monterey coal, Figure 2. In this instance, the two lower curves are not parallel. However, the conversion in 2-methylnaphthalene shows approximately proportional dependence on tetralin concentration whereas in the pyrene-tetralin-H₂ system there is again a major increase in conversion with as little as 15% tetralin.

It has previously been reported that the presence of molecular hydrogen can increase coal conversion in solvents which have low donor capacity (3). The data presented here confirm these findings and also demonstrate that the effect of hydrogen gas is dependent upon the chemical structure of the other compounds present. In particular, the combination of a polycondensed aromatic (pyrene) with a donor in the presence of hydrogen behaves synergistically with respect to coal conversion.

Effect of Hydrogen Pressure

The influence of hydrogen pressure on the conversion of the two coals is shown as a function of donor concentration in Figure 3. The pressures examined were 1000 and 1800 psig.

There was no apparent effect due to hydrogen pressure, over this range, for the conversion of Belle Ayr coal. However, with Monterey coal, the effect of increasing pressure was to increase the conversions in pure pyrene and to some extent, in pyrene-tetralin mixtures to that obtained in pure tetralin. From the standpoint of maximizing conversion of Monterey coal, at high hydrogen pressure, there is little benefit to be derived from the addition of tetralin. This is not to state that the quality of the liquefied products is independent of donor concentration.

The effects of hydrogen pressure during coal conversion have been reported for the Exxon EDS process when operating in a mode where vacuum tower bottoms were recycled (4). Such a recycle stream would be expected to contain a proportion of polycondensed aromatics and compounds with similar chemistry. It was found that increasing the hydrogen pressure from 1500 to 2500 psig gave improved conversion and improved selectivity to lighter products for a range of coals including ones similar to those reported here.

The different responses of the two coals studied here may be partly attributable to differences in their respective mineral matter compositions. It has been

reported that the hydrogenation of pyrene is related to the coal pyritic iron content (2) which is much higher for the Monterey coal.

Hydrogen Transfer

It is commonly known that the extent of coal conversion is related to the hydrogen consumed in the process. Under given reaction conditions, the quantity of hydrogen required is independent of solvent composition. At any given time, the majority of hydrogen is supplied by the most labile source.

It may be assumed that, in the systems described, tetralin is the preferred hydrogen source. For each experiment, the amount of hydrogen made available by tetralin dehydrogenation was calculated, correction being made for isomerization to methylindan. It was found that in the pyrene-tetralin-H₂ system, less hydrogen was made available by tetralin dehydrogenation than in pure tetralin for a comparable conversion level. At lower tetralin concentrations in the mixed solvents, it does not appear that the amount of tetralin was a limiting factor since its dehydrogenation to naphthalene was always less than 40%. Supporting this contention earlier studies (1) have shown that a variation of tetralin concentration from 4 to 43 wt% in Monterey coal conversion, resulted in similar conversions but with corresponding tetralin dehydrogenations of 86 to 8% respectively.

The relative effect of the other solvent component and the gas atmosphere on hydrogen transfer from tetralin is shown in Figure 4 for both coals at a selected level of conversion. In these examples, the tetralin concentration differs since, as shown on Figure 1 and 2, the required concentration to attain a particular conversion is dependent upon the other system components. It can be seen that the required donor capacity for coal conversion is dependent upon the nature of the coal and of the other components present. The implication is that there is considerable potential for economy in donor consumption by judicious control of the solvent composition.

From the previous work with pyrene alone (2) it seems probable that the reduced hydrogen transfer from tetralin is due to part of the hydrogen demand being met by the transfer of molecular hydrogen to the coal through the formation of dihydropyrene. Such a mechanism is not as readily available with 2-methylnaphthalene as it is more difficult to reduce with hydrogen. There was no evidence of the presence of 2-methyltetralin in the reaction products where 2-methylnaphthalene was used as a solvent component.

Thermal Reaction of Pyrene and Tetralin

Some experiments were conducted to investigate the reactions between pyrene, tetralin and hydrogen gas in an attempt to elucidate reasons for the observed synergism. The results are summarized in Table 2 and show the extent of pyrene hydrogenation under the different conditions studied.

It can be seen that pyrene was thermally hydrogenated by reaction with hydrogen gas and under these conditions, its conversion to dihydropyrene was low (0.6%). The extent of hydrogenation was increased by the addition of iron pyrites. These findings are consistent with previous results relating conversion in pyrene to coal mineral matter catalysis (2).

In an inert atmosphere, in the presence of tetralin, 5.7% of the pyrene was hydrogenated. This result is particularly significant as it establishes that tetralin can transfer hydrogen to pyrene producing a substantial concentration of a more active donor. The same experiment conducted under molecular hydrogen resulted in a still greater degree of pyrene hydrogenation which was higher than would be predicted from a purely additive effect.

The foregoing results suggest that there may be several different mechanisms to effect H-transfer in systems which contain donors and polyaromatic compounds. Some possible alternatives are discussed below.

Neglecting direct interaction of hydrogen gas with coal derived free radicals, there appear to be four possible routes for H-transfer:

- 1) Tetralin + R → Naphthalene + R-H
- 2) Tetralin + Pyrene → Naphthalene + Dihdropyrene
- 3) Pyrene + H₂ → Dihdropyrene
- 4) Dihdropyrene + R' → Pyrene + R-H

Reaction 1) is the conventionally regarded process of hydrogen transfer from a donor. Reaction 2), it has been shown, can take place thermally and is promoted by molecular hydrogen. Reaction 3) can occur thermally and is catalyzed by coal mineral matter. Reaction 4) is parallel to reaction 1) and presumably proceeds at a faster rate.

In pure tetralin, reaction 1) prevails and in pure pyrene, reactions 3) and 4) take place. In pyrene-tetralin mixtures under hydrogen, all four reactions are possible and on this basis an explanation for the observed synergism in conversion and for the reduction in hydrogen transferred from tetralin is proposed.

The combined effect of reactions 2) and 3) is to generate a higher concentration of dihydrodropyrene than when 3) alone is possible. Dihdropyrene would be preferred to tetralin as the hydrogen donor since it has been shown that depletion of donors is essentially sequential (1). That is, until the most active donor is reduced to a low level, there is little significant contribution from the next most labile hydrogen source.

The ensuing increase in dihydrodropyrene concentration due to H-transfer from a low concentration of tetralin, especially in the early stages of reaction, could account for the observed synergism. In addition, some of the net hydrogen demand will be met via reaction 3) which will reduce the amount of hydrogen which otherwise would be predominantly supplied by the tetralin. It is anticipated that economies in donor concentration and consumption observed in these model compound studies would be observed in a process such as EDS when operating with bottoms recycle.

This explanation is tentative and there are many other factors which have not been considered, among which are the differences in solubility and dispersive properties of pyrene and tetralin and their mixtures. The outcome of these studies shows that there are potential advantages to coal liquefaction through an improved understanding of solvent chemistry which can lead to the selection and control of solvent composition. Some benefits of selected solvent recycle have already been observed in practice (4, 5, 6) and improvements such as those found in these model compound mixtures could significantly affect the viability of a coal liquefaction process.

SUMMARY

Studies of coal conversion in mixtures of pyrene, 2-methylnaphthalene and tetralin have shown that:

- 1) Mixtures of pyrene and tetralin in the presence of hydrogen gas have been found to be synergistic in coal conversion. At tetralin concentrations as low as 15 wt%, the conversion was almost as high as that in pure tetralin.
- 2) There is no similar synergistic effect when 2-methylnaphthalene is substituted for pyrene. The ease of reduction of pyrene is considered to be one reason for this different behavior.
- 3) With pyrene-tetralin mixtures in hydrogen, the hydrogen supplied by the donor at a given level of coal conversion is considerably reduced.
- 4) Reactions between pyrene, tetralin and hydrogen gas in the absence of coal showed that pyrene can be hydrogenated by reaction with molecular hydrogen alone and by tetralin alone. In combination with tetralin and hydrogen, the extent of pyrene hydrogenation is further enhanced.

ACKNOWLEDGEMENT

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Table 1
Properties of Coals

	<u>Belle Ayr</u>	<u>Monterey</u>
Elemental Analysis (m.f.)		
% C	72.20	75.18
H	5.65	5.82
O	20.56	12.78
N	1.19	1.38
S	0.40	4.34
Ash	4.50	11.19
Sulphur Forms		
Pyritic	0.03	0.68
Sulphate	0.03	0.75
Organic	0.35	2.97
Total	0.41	4.40

Table 2
Thermal Reactions of Pyrene, Tetralin and Hydrogen

Solvent	Gas	Time (mins)	Temp (°C)	Pressure (psig)	% Pyrene Conversion to Dihdropyrene
Pyrene	H ₂	60	400	1000	0.6
92% Pyrene/8% Iron Pyrites	H ₂	60	400	1000	2.5
50% Pyrene/Tetralin	Ar	60	400	1000	5.7
50% Pyrene/Tetralin	H ₂	60	400	1000	8.6

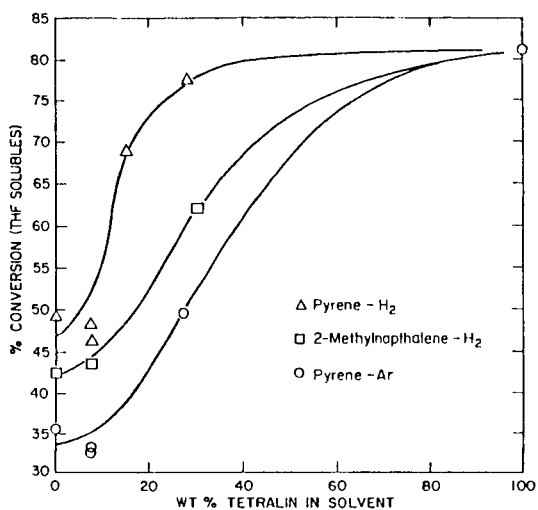


Figure 1. Conversion of Belle Ayr Coal in Donor-Non-Donor Solvent Mixtures (400°C, 1 hr, 1000 psig)

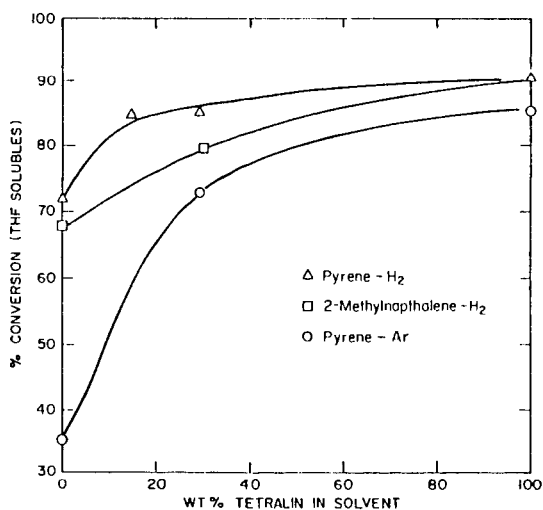


Figure 2. Conversion of Monterey Coal in Donor-Non-Donor Solvent Mixtures (400°C, 1 hr, 1000 psig)

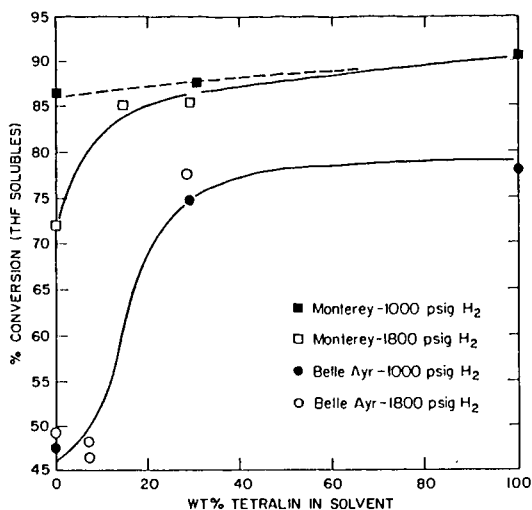


Figure 3. Effect of H₂ Pressure on Coal Conversion in Donor-Non-Donor Solvent Mixtures (400°C, 1 hr)

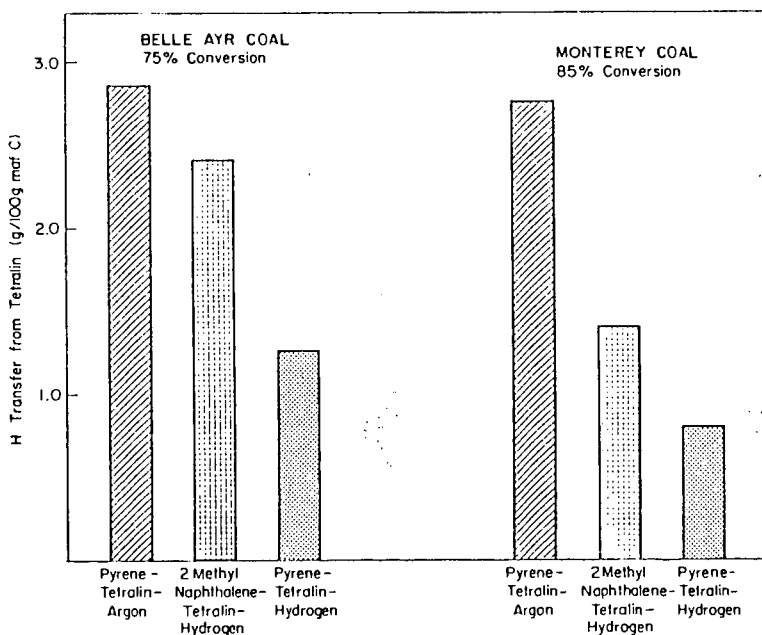


Figure 4. Effect of Solvent and Gas Atmosphere on Hydrogen Transfer (400°C, 1 hr, 1000 psig)

Evaluation of the Donor Ability of Coal Liquefaction Solvents

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INTRODUCTION

Hydrogen donor solvents are used in most processes for the direct liquefaction of coal. The overall performance of these solvents depends on several qualities, including the abilities to physically solvate coal and its liquefaction products, to hold coal particles in suspension, to assist transfer of hydrogen from the gas phase to coal by dissolving molecular hydrogen or undergoing hydrogenation/dehydrogenation cycles (hydrogen shuttling), and to donate hydrogen directly to coal. Unknown factors may also be involved. In addition, in the case of commercial application, the solvents must be derived from coal and be suitable for recycle operation as well. In order to fully understand the function and importance of liquefaction solvents, the influence of each property must be studied separately. As a step towards this goal, we have developed a method by which the relative hydrogen donor ability of liquefaction solvents may be evaluated.

Our method of evaluation is based on a generally accepted hypothesis of the mechanism of coal liquefaction that has been used to rationalize the kinetics of coal liquefaction (1,2) and has been discussed several times in recent reports (for example (3,4,5)). According to this mechanism, the initial act is rupture of the weaker covalent bonds in coal. This produces two free radicals in close proximity. These radicals may either abstract hydrogen from any available source (donor solvent, coal or molecular hydrogen), undergo rearrangement, or add to some other site on either coal or solvent. Recombination or addition may lead to production of insoluble or char-like residues that are clearly undesirable. One critical function of the donor solvent is to provide a source of hydrogen. Abstraction of hydrogen by coal-derived free radicals prevents retrogressive reactions that lead to higher molecular weight products, and it directs more coal along the desired pathways to lower molecular weight products. Thus, donors with high potential for hydrogen transfer are regarded as beneficial to increased liquefaction yields.

Our approach to evaluation of the donor property was to devise a test that embodies the main features of the free radical mechanism of coal liquefaction. The basic idea is shown in Figure 1. Benzyl radicals are generated by the thermolysis of a convenient precursor at relatively low temperatures. These radicals then behave like the free radicals generated by the thermolysis of coal at liquefaction temperatures. When benzyl radicals are generated in a donor solvent, the relative amounts of toluene and bibenzyl produced reflect the relative ability of the solvent to donate hydrogen and to prevent recombination. A variable amount of benzyl radical is also lost, which presumably represents that amount which adds to or combines with the solvent.

As precursors to benzyl radical, we have used both dibenzylidiazene and dibenzylmercury. Both decompose at convenient rates at moderate temperatures (130-170°C) (6,7). The initially formed reaction products were found to be stable at these relatively low temperatures. Thus their yields, determined after decomposition of the precursor, represent the actual quantities of products formed as a result of the primary reactions.

Other methods have been used in the past to provide a "solvent quality index." Notably, measurement of liquefaction yields produced under specified conditions and with a specified coal has been used to provide a direct empirical evaluation of solvent quality (8,9).

Various spectroscopic methods have also been used to estimate the relative amount of benzylic or hydroaromatic hydrogen available for transfer (10,11,12). These methods serve their intended purposes well. In the present work, we aim at developing a better understanding of the chemistry of liquefaction and the overall performance of liquefaction solvents by isolating the hydrogen donor ability and free radical scavenger ability for study.

RESULTS AND DISCUSSION

Since many of the compounds to be tested as model hydrogen donors are solids at room temperature, it was worthwhile to use an inert liquid as a diluent. Tert-butylbenzene served this purpose well. It possesses only relatively inert aromatic and primary aliphatic hydrogen and sufficient solvent power to dissolve most of the donor solvents to be tested. Decomposition of either benzyl radical precursor in tert-butylbenzene solution produced only small yields of toluene.

Material balance studies showed that not all of the benzyl radical present in the precursor was recovered as either toluene or bibenzyl. A sizeable fraction is apparently removed by side reactions with the solvent. In pure t-butylbenzene, this accounted for 24% of the benzyl radical, while in a 50/50 wt mixture of t-butylbenzene and tetralin, it accounted for 32%. In the gas chromatograms of the decomposition products, new peaks appeared which were due to high boiling compounds. In the case of runs done in the presence of tetralin, GC/MS analyses indicated that three of these peaks had the correct molecular weights for benzyltetralins, benzylnaphthalene and bitetralyl. These products must arise from radical combination and addition reactions.

The appearance of solvent combination and addition products is in accord with some recently reported⁴ results from other groups. Collins et. al. (13) reported that after they heated coal with ¹⁴C labeled tetralin at 400° C for 1 hour, the pyridine solubles were 1.6 wt. percent tetralin and the residue 2.6 wt. percent tetralin. In another experiment (13), ¹⁴C labeled 1,3 - diphenylpropane was heated with tetralin at 400° C for 1 hour. Toluene and ethylbenzene were major products. In addition, methylnaphthalenes, methylidihydronaphthalenes, phenylethyltetralins, and phenylethyl naphthalenes were found. A mechanism was proposed that involved combination of phenylethyl with tetralyl radical, followed by further thermolysis to produce methyl substituted tetralins and naphthalenes. Thus at higher temperatures, radical addition to solvent may be followed by subsequent thermolysis of the newly formed bridge. Evidence for the addition and subsequent dissociation of benzyl radical with tetralin at temperatures of 400-450° C has also been reported by workers at Gulf (14). Another piece of evidence showing the importance of addition reactions is the report (15) that negative solvent balances were found during preheater studies. These findings were interpreted to mean that during the initial phase of liquefaction (300° - 400° C), coal-derived solvent became bound to the coal so tightly that it could not be freed by either distillation or solvent extraction. Subsequent reaction after reaching 450° C changed the solvent balance to positive. Processes analogous to the addition/dissociation reactions described by Collins may be involved.

Taking this evidence together, it is apparent that an additional mode of action of donor solvent is that of free radical scavenger by combination and addition reactions. Accordingly, three indices were devised to compare donor solvents; the donor, the scavenger, and the combined index.

$$\text{Donor Index} = \frac{\text{Toluene}}{2 \text{ Precursor}}$$

$$\text{Scavenger Index} = \frac{2 \text{ Precursor} - (\text{Toluene} + 2 \text{ Bibenzyl})}{2 \text{ Precursor}}$$

$$\text{Combined Index} = \frac{\text{Precursor-Bibenzyl}}{\text{Precursor}}$$

These indices are based on mole ratios.

Since the combined index is merely the sum of the other two, we really have two independent measures of two different solvent qualities. The donor index may be taken as the relative amount of benzyl radical which abstracts hydrogen, and the scavenger index as the relative amount of benzyl radical which adds in some manner to the solvent. The scavenger index is determined by difference, being that fraction of benzyl which does not appear as toluene or dibenzyl.

Initial experiments were carried out with dibenzylidiazene and a series of model donor compounds. Although we were able to obtain satisfactory data with dibenzylidiazene, we have come to prefer using dibenzylmercury because it is far more stable in storage. We have found that dibenzylidiazene decomposes spontaneously over the course of several days by various pathways. This instability made it necessary to prepare the diazene immediately before use and to assay its purity by determination of the amount of nitrogen evolved upon decomposition of a known weight of crude material. By contrast, dibenzylmercury may be stored without significant decomposition for months. Thus with dibenzylmercury, the amount of benzyl added to each reaction mixture could be carefully controlled and was usually held constant at 0.87 wt. percent, based on the hydrocarbon portion of the precursor.

The three solvent indices were determined for the decomposition of dibenzylmercury for several solvent mixtures made from different amounts of tetralin in *t*-butylbenzene. The data contained in Figure 2 show that the donor index increases with increasing tetralin concentration. Also shown in this figure are data taken from reference (16) for conversion of a bituminous coal to pyridine soluble material after reaction for three minutes at 427°F in mixtures of tetralin with methylnaphthalene, cresol, and picoline. Conversion as well as the donor index goes up as the tetralin concentration in the solvent increases. This comparison is made only to point out the qualitative similarity between the two results since we assume that both coal conversion and toluene yield are related to the relative hydrogen donor ability of the solvent. In both cases the greatest increase in conversion or toluene yield comes at relatively low tetralin concentration.

The series of model compounds in Table I were evaluated using dibenzylidiazene as the source of benzyl radical. In each case the donor was diluted to 50 wt. percent in *t*-butylbenzene. These data show that the donor ability as measured by this method is indeed variable. The relative order of donor ability of the hydrocarbons is mostly as expected. Both hydroaromatic compounds—tetralin and 9,10-dihydrophenanthrene—are distinctly better than either *t*-butylbenzene or 1-methylnaphthalene. Indan has the highest donor index of the hydrocarbons in Table I. This is noteworthy in view of the prejudice often voiced against indanyl structures. Rearrangement of hydroaromatic compounds in recycle solvents to indanyl structures is often said to be detrimental. However, indan seems to be a good rather than poor donor, although its capacity to shuttle hydrogen by dehydrogenation cycles is still open to question.

In the first case, the donors in Table I have been compared at equivalent weight percent concentrations. This relates more directly to their use in practice and is more convenient when making comparisons among actual coal-derived solvents. However, if the assumption is made that essentially all hydrogen donated comes from benzylic sites, the donor index may be expressed on the basis of the molal concentration of benzylic hydrogen. The molal donor indices shown in Table I should relate more directly to the reactivity of individual benzylic hydrogens than does the simple donor index. In this comparison, benzylic hydrogen on indan is ranked between those on dihydrophenanthrene and tetralin. An important factor contributing to indan's superior rank measured on a weight basis is that benzylic hydrogen accounts for a relatively larger fraction of its weight.

The heteroatomic substituted compounds in Table I are also found to be relatively good donors, with the exception of tetrahydroquinoline. A striking aspect of this data is that the heteroatomic compounds all have relatively high scavenger indices. Their combined indices are therefore distinctly higher than any of the hydrocarbon species. Said another way, the

yields of the product of recombination, bibenzyl, are found to be smaller in the presence of these heteroatomic compounds than in the hydrocarbons. Tetrahydroquinoline has been reported to be a superior solvent for coal liquefaction (17,18). Also, esr experiments have shown that the concentration of free radicals in mixtures of coal and solvent after treatment at liquefaction conditions was roughly a factor of six smaller in the case of tetrahydroquinoline (or tetralin) than naphthalene (19). Tetrahydroquinoline's superior quality has been attributed to a unique combination of readily donatable hydrogen with a heightened ability to solvate coal and its liquefaction products due to the presence of both aromatic and polar functionality. In view of its high scavenger index, an additional reason for the superior liquefaction performance of tetrahydroquinoline may be its ability to add to or combine with free radicals initially produced by the thermolytic reactions of coal.

Table 2 contains the donor indices obtained for several coal-derived liquefaction solvents selected to provide a range of quality from poor to satisfactory. In all of these cases, the scavenger index could not be obtained because the bibenzyl peak was buried within the broad envelope of unresolved peaks usually associated with gas chromatograms of coal-derived liquids. All of the donor indices in Table 2 were obtained using dibenzylmercury as the source of benzyl radical. Note that in this case the donor index for tetralin is somewhat different than that in Table 1. We attribute this to the change in precursor from diazene to mercurial. The precision of both determinations is about the same.

Anthracene oil, cresote oil, and Panasol are generally considered poor performers in coal liquefaction. They also have the lowest donor indices in Table 2. Panasol is not a coal-derived liquid, but it is largely made up of mono-, di-, and tri-methyl-naphthalenes, which are frequently also major components in coal-derived liquids. Its donor index is essentially the same as that found for methylnaphthalene. By comparison, the index determined for a distillate cut from a SRC-II recycle solvent is higher, although not as high as that for tetralin.

Comparison of the donor indices with other available quality criteria is made with two sets of solvents. The DCD series are recycle solvents derived from Blacksville coal under different processing conditions in the 1000 lb/day liquefaction unit at PETC. The values of IR were derived as recommended (10) from the ratio of absorbances at 3040 and 2930 cm^{-1} due to aromatic and aliphatic hydrogen, respectively. Higher ratios reflect a greater degree of hydrogenation or relative aliphatic hydrogen content. In this comparison, there is a qualitative agreement between the two methods. That is, the donor index increases with the degree of hydrogenation of the recycle solvent.

The second set of solvents—F2, F14, and F16—provide a comparison of liquefaction yield versus donor index. In this case, liquefaction yield refers to benzene soluble yield from Wyodak coal after heating to 440°C and immediately cooling in a two liter autoclave under hydrogen pressure (2000 psi, cold) at a 2/1 solvent-to-coal ratio (20). F2-HV is the 500°F + distillation residue from a lightly hydrogenated recycle oil made in the Wilsonville SRC pilot plant from Wyodak coal. F-14 is a lightly hydrogenated recycle oil made in the Tacoma SRC pilot plant from Kentucky coal. F-16 is a coal gasification tar from an in situ gasification project near Hanna, Wyoming. These three solvents were selected because the liquefaction yields clearly distinguish the order $F14 > F2 > F16$. The donor indices are in the same order. However, the reported IR values (20) are not in this order. The relatively high IR values and results from other methods of characterization (20) indicate that all of these solvents, F16 in particular, are highly hydrogenated. In this case, the optimum hydrogen content may be closer to that of F14. Hydrogenation of solvents beyond certain limits has been shown to be detrimental because aliphatic structures begin to replace hydroaromatic structures (16,20).

Taken together, these data indicate that there is good qualitative agreement between liquefaction performance and the donor index. The ability of solvents to donate hydrogen to a free benzyl radical is an indication of how well they may donate to a typical free radical site formed on coal during liquefaction. We are now developing refined methods designed to yield more quantitative comparisons among hydrogen donor solvents.

EXPERIMENTAL










MATERIALS: All compounds that were purchased were reagent grade or equivalent and were used as received except as noted. Tetrahydronaphthalene (Tetrafin, Fisher) was trickled through a dry-packed column of activated alumina immediately before use and stored under argon. This treatment removed and prevented reformation of tetralin hydroperoxide and tetralone, which had been found to be present in all tetralin samples received. Dibenzylmercury (ALFA) was recrystallized once from absolute ethanol (m.p. 109-110° uncorr) and vacuum dried before use.

METHODS: Bis (phenylmethyl) diazene was prepared according to established procedures by the oxidation of N,N'-dibenzylhydrazine with freshly prepared mercuric oxide. (21,22). The diazene decomposes in air at room temperature but could be stored over a period of weeks at -10°C under argon. It was necessary to assay it before each use. This was done by measuring the nitrogen evolution on thermolysis in *t*-butylbenzene at 170°C. A mercury filled gas buret and leveling bulb proved satisfactory and gave a precision of about 2% absolute. Benzyl radicals were generated by thermolysis of either dibenzylmercury (7) or bis (phenylmethyl) diazene in a reaction vessel at selected temperatures between 130 and 210°C. The radical precursor was present at concentrations of 1-2 wt.% in various mixtures of donor solvents and *t*-butylbenzene. Each vessel was assembled from a 1/2" 316SS swagelock union and two end plugs and had a capacity of about 2 mL. The vessels were sealed after loading and maintained at temperature in a convection oven for 12-16 hours to ensure complete decomposition of the radical precursors. Product analyses were carried out on a HP5830 gas chromatograph with a six foot carbowax 20M (10% on chromosorb W) column, using internal standards. Each sample was analyzed in duplicate. Several unknown peaks were identified on a DuPont 21-490 MS after separation by an attached Varian 3700 G.C.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of their colleagues at PETC, especially Charles Schmidt for obtaining the GC/MS analysis, Donald Krastin and John Ruether for providing samples from the operation of the 1 tpd liquefaction unit, and Sidney Friedman for helpful discussions. We are also indebted to Prof. Howard Silver of the University of Wyoming for providing samples of donor solvents.

TABLE I. SOLVENT INDICES OF MODEL HYDROGEN DONOR SOLVENTS*

COMPOUNDS	DONOR	SCAVENGER	COMBINED	DONOR/ α -CH**
	0.09	0.24	0.33	
	0.27	0.32	0.59	0.0178
	0.31	0.23	0.53	0.0279
	0.35	0.30	0.65	0.0207
	0.13	0.45	0.58	0.0123
	0.18	0.62	0.81	
	0.32	0.46	0.78	
	0.28	0.56	0.84	
	0.40	0.41	0.81	

*Determined by decomposition of dibenzylidiazene in solvent mixtures composed of 50/50 wt/wt of t-butylbenzene and donor. Estimated precision is ± 0.02 , based on triplicate determinations for tetralin.

**Donor index divided by molal concentration of benzylic hydrogen.

TABLE 2. DONOR INDICES OF COAL-DERIVED LIQUEFACTION SOLVENTS

<u>SOLVENT</u>	<u>DONOR INDEX*</u>	<u>\overline{IR}</u>	<u>LIQUEFACTION YIELD**</u>
Tetralin	0.41		
Anthracene Oil	0.21		
Creosote Oil	0.17		
Panasol	0.14		
SRC-II Distillate	0.31		
DCD 12/1	0.24	2.2	
DCD 12/26	0.28	2.7	
DCD 13/5	0.24	2.0	
F2-HV	0.32	9.2**	83.6
F14	0.45	6.1**	93.6
F16	0.29	12.7**	63.2

*Obtained using dibenzylmercury in 50 wt. per cent solutions with t-butylbenzene.
Precision (2σ) estimated as ± 0.03 based on six replicates.

**Values taken from Reference 20.

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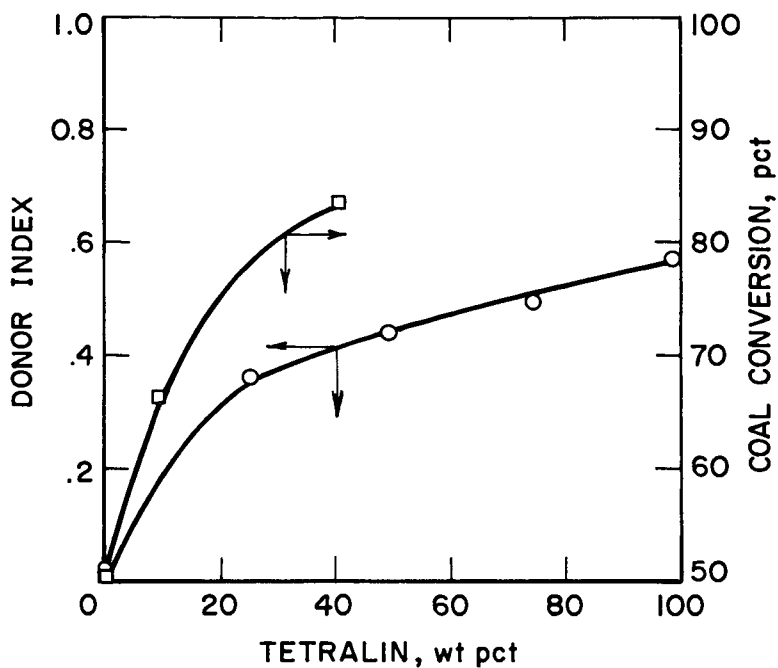


Figure 2.- Donor index of Tetralin/t-butylbenzene mixtures, ○, and coal conversion in synthetic solvents of different tetralin concentration, □, (from ref. 11).

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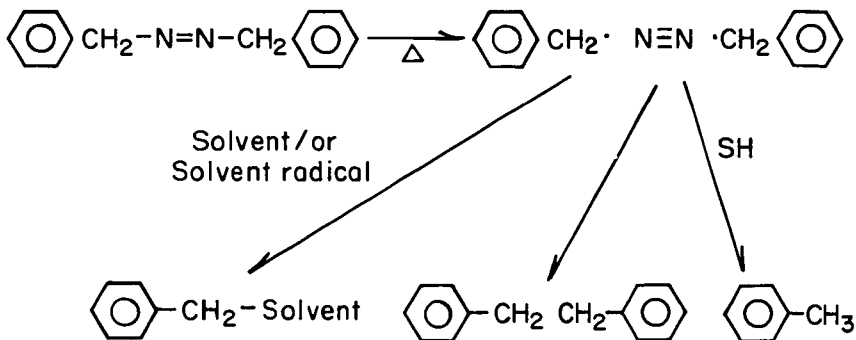
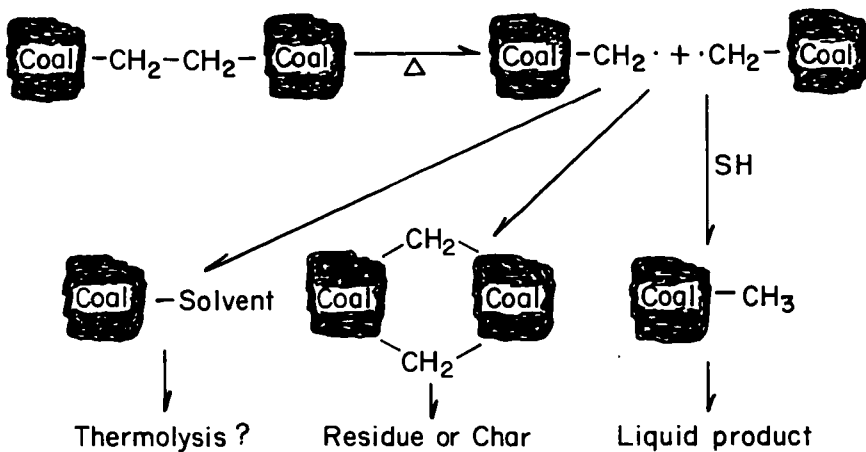


Figure 1.- Simplified hypothetical mechanism of coal liquefaction and its analog.

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RADICAL PATHWAYS OF COAL DISSOLUTION IN DONOR MEDIA DURING REACTIONS OF COALS AND SPECIFICALLY DEUTERATED TETRALIN*

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INTRODUCTION

Recent studies utilizing deuterium labelling to trace the pathways of hydrogen transport between donor solvent, coal, and model compounds in the laboratories of Professor Leon Stock (Univ. of Chicago), Drs. L. A. Heredy, R. P. Skowronski and J. J. Ratto (Rockwell International) and in our own laboratory promise to provide a detailed understanding of mechanistic pathways operating at the molecular level during coal dissolution in donor media. Deuterium scrambling in donor solvents constitutes a sensitive probe of the structural features of coal and mineral matter. In previous papers^{1,2} we presented detailed information concerning the time dependence of the structural distribution of deuterium transferred to a subbituminous coal at 427°C in tetralin-1,1-d₂. In a preliminary report³ of our recent studies of high temperature reactions of specific radicals in the tetralin and alkylindan systems we presented evidence that 2-tetralyl as well as 1-tetralyl radical is formed during the oxidation of tetralin to naphthalene. The evidence for the intermediacy of 2-tetralyl was the observation of scrambling of deuterium from the 1- to the 2-position of tetralin during reaction with coal. In this paper we present a study of the scrambling and depletion of deuterium in reactions of a bituminous and a subbituminous coal with tetralin-1,1-d₂. Radical and ionic pathways responsible for major differences in scrambling rates for the two coals are discussed.

EXPERIMENTAL

Materials

Two coals were used in this study: Illinois #6 (Monterey) bituminous coal (C, 76.8%, H, 4.8%, S, 3.2%, N, 1.61% dry maf basis, 4.8% ash) and Kaiparowitz subbituminous coal (C, 77.3%, H, 1.2%, S, 0.8%, N, 1.2% dry maf basis, 8.5% ash). The coals were ground to -300 U.S. mesh and dried at 80°C and 10⁻² Torr.

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Tetralin-1,1-d₂ was prepared as described previously² except that the byproduct dihydronaphthalene was removed by treatment of the mixture of tetralin-1,1-d₂ and dihydronaphthalene with sufficient Br₂ to consume dihydronaphthalene followed by distillation of the lower boiling tetralin.

Procedure for the Reactions of Coals and Tetralin-1,1-d₂

Coal (0.75g) and Tetralin (1.5g) were loaded in a 3 in x 3/8 in Swagelok-capped type 316 stainless steel tube. The tube was plunged in a molten lead bath maintained at a suitably higher temperature such that the bath would attain the desired temperature (427 ± 5°C) within approximately one minute. The tube was withdrawn after the desired reaction time, quenched in water, and worked up as follows: The contents of the tube were washed into a beaker with tetrahydrofuran (THF), ca. 75 ml. The THF solution and fines were centrifuged for several minutes. The THF solution was decanted and the fines washed and centrifuged two more times to remove soluble material. The THF solutions were combined and concentrated to ca. 2 ml and added to 250 ml of pentane above a 0.45 µm Millipore filter. The preasphaltenes and asphaltenes precipitated and were collected on the filter and washed with three portions of pentane. Small portions of the pentane solutions were saved for gc analysis to determine methylindane, tetralin, and naphthalene yields. The pentane solutions were concentrated to an oil in a small flask which was attached to a short path vacuum distillation apparatus and tetralin, naphthalene and methylindane et al. were removed at 150°C and 10⁻¹ Torr, leaving the light oils behind. The tetralin/naphthalene mixture was separated into its components by preparative gc or by preparative liquid chromatography.

Deuterium Analysis

Isolated tetralin and naphthalene were first examined by proton-decoupled ²H Fourier transform nuclear magnetic resonance (FTNMR) spectroscopy (12.211 MHz) using a Varian model FT-80 instrument. The tetralin samples were then spiked with toluene-d₈ and reexamined by ¹H FTNMR. The toluene methyl resonance lies conveniently resolved between the two aliphatic resonances of tetralin. The toluene-d₈/tetralin ratio as determined by gas chromatography (gc) was used in conjunction with the toluene-d₈/tetralin FTNMR integral ratios to calculate the total isotope level in the recovered tetralin. The recovered tetralin and naphthalene were also examined by gc/mass spectrometry to determine the distribution of labeled species.

RESULTS AND DISCUSSION

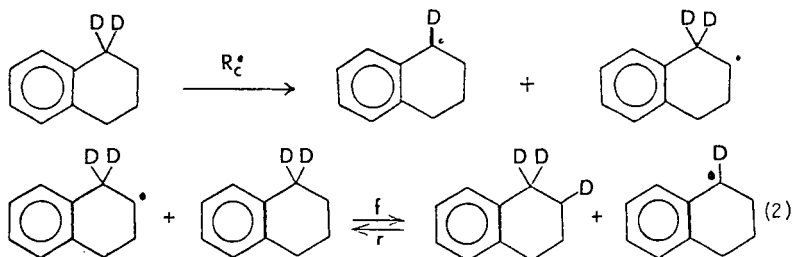
The distributions of deuterium label in the recovered tetralin and naphthalene are shown in Table 1. For Kaiparowitz coal, deuterium in the 1-position of tetralin decreases from 100% to 78% after 60 minutes' reaction. For Illinois No. 6, the deuterium content falls from 100% to 39% after 60 minutes, and the degree of scrambling is greater after only 5 minutes than the 60 minute reaction of Kaiparowitz. Incorporation of deuterium in the 2-position of tetralin to the extent of 11% occurs in 5 minutes with Illinois No. 6 but required 60 minutes with Kaiparowitz. A completely random distribution of deuterium would lead to 33% label in each of the aromatic 1- and

2-positions. The Kaiparowitz reaction was well short of complete scrambling at 60 minutes, but the Illinois No. 6 approaches complete scrambling at 35 minutes.

The exchange of deuterium between coal and tetralin occurs in both cases. Table 2 shows that about 25% of the label is lost from tetralin for either coal in 60 minutes. The rate of label loss appears slightly faster for Illinois No. 6 in the shorter reaction times. The total hydrogen uptake by the two coals, as measured by the conversion of tetralin to naphthalene, is identical for the two coals at 10 minutes' or less reaction time (Table 3). The Illinois No. 6 coal consumes slightly more hydrogen at long reaction times. This method is in error probably by about 3-5% of naphthalene yield since some tetralin becomes chemically bonded to fractions of the coal. It is further noted that the yields of 1-methylindan are only slightly greater at longer reaction times for Illinois No. 6.

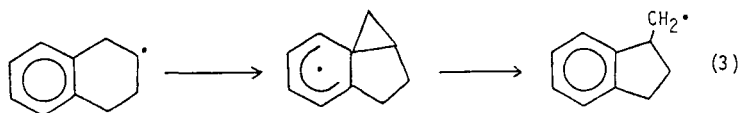
It is clear from these results that the degree of oxidation of tetralin at short reaction times is similar for the two coals and that both coals undergo label exchange with the coal, reminiscent of the results of Skowronski, Heredy and Ratto.⁴ The dramatic increase in scrambling rates induced by Illinois No. 6 coal at equal degrees of oxidation of the tetralin almost certainly indicates a different scrambling mechanism than that occurring with Kaiparowitz Coal.

In the conventional picture of coal dissolution, unimolecular cleavage of weaker C-C, C-S and C-O bonds in the coal leads to free radicals (eq. 1) which abstract hydrogen from the coal or donor solvent, or undergo disproportionation, combination, fragmentation and addition reactions, and participate in chain decompositions of hydrocarbons.



Ignoring the participation of phenolic or sulfur groups in the coal for the moment, the formation of 2-tetralyl and its subsequent reaction with the solvent (eq. 2) will lead to deuterium label in the 2-position. We have demonstrated⁵ in a study of high temperature reactions of tetralyl and indanylmethyl radicals that the 1-methylindan observed in the reactions of

coal and tetralin is a product of the reverse 1,2-aryl migration of 2-tetralyl radical (eq. 3).



This reaction is endothermic with an activation barrier of 22 ± 2 kcal/mole.⁵ The presence of 1-methylindan in coal reactions indicates that coal derived radicals are sufficiently non-selective to produce 2- as well as 1-tetralyl radicals.³ A second pathway of scrambling is the reverse of eq. 2. Reaction (2f) proceeds with $\Delta G = 0.1$ kcal/mole and $\Delta H = -16.1$ kcal/mole at 427°C , from thermochemical estimates of thermodynamic properties of 1- and 2-tetralyl radicals. Thus, although the reaction is slow, equal concentrations of 1- and 2-tetralyl radical would exist at equilibrium at 427°C . The direct unimolecular interconversion of 1-tetralyl and 2-tetralyl radicals is predicted not to occur due to the net antibonding configuration of the 1,2-hydrogen atom shift intermediate.⁷ Of course, 1,2-hydrogen shifts and alkyl shifts in carbonium ions proceed through a net bonding intermediate and occur very rapidly.

Thus, constituents of the coal which could convert radicals (which undergo relatively inefficient bimolecular interconversion) to carbonium ions (which undergo very rapid unimolecular rearrangements), would cause significant enhancements in scrambling rates. A likely candidate for the conversion of radicals to carbonium ions is the pyrite in Illinois No. 6 coal. Illinois No. 6 contains about 3% sulfur, two-thirds of which is associated with iron. By contrast, the low-sulfur Kaiparowitz contains only 40 ppm of iron. Reaction of Fe^{3+} with solvent radicals may lead to the corresponding carbonium ions



which would rapidly equilibrate the 1- and 2-hydrogens of tetralin. Consistent with this view, Bockrath has observed an enhanced rate of isomerization of tetralin to 1-methylindan with added pyrite. Whitehurst, et al, have observed that pyrite catalyzes solvent isomerization, dehydrogenation, and hydrogen transfer, though pyrite is by no means the only active catalytic agent.¹⁰ The form of iron is not specified in eq. 4. The oxidation of radicals by Fe^{3+} in aqueous media is well known.¹¹ However, more work is needed to identify the structure and mechanisms of the iron sulfide participation in

nonpolar donor media. Further work is underway in this laboratory to identify the structural features of coals which enhance hydrogen shuttling.

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TABLE 1.

DEUTERIUM LABEL DISTRIBUTIONS IN RECOVERED TETRALIN AND NAPHTHALENE

Coal	Reaction Time	Tetralin ^a		Naphthalene ^b	
		Arom	1 2	1 2	
Illinois No. 6	0	0	100	0	-- --
	2.5	5.6	91.8	2.5	91.3 8.7
	5.0	30.0	55.2	0.8	78.3 21.7
	10.0	29.9	51.7	18.4	74.6 25.4
	35.0	35.7	39.3	25.0	54.8 45.2
	60.0	36.6	38.8	24.6	59.1 40.8
Kaiparowitz	0	0	100	0	-- --
	10	2.5	95.4	2.1	45.1 4.9
	35	4.2	90.2	5.6	92.0 8.0
	60	10.9	78.2	10.9	87.5 12.5

^a % of deuterium in the aromatic, 1-, or 2-position^b % of deuterium in the 1- or 2-position

TABLE 2

ISOTOPE DEPLETION IN RECOVERED TETRALIN

Coal	Reaction Time, min	Deuterium Atoms/Molecule ^a
Illinois No. 6	0	2.0
	2.5	1.88
	5.0	1.64 ^b
	10.0	1.22 ^b
	35.0	1.68
	60.0	1.45
Kaiparowitz	0	2.0
	10	1.82
	35	1.56
	60	1.52

^a \pm 0.2 Atoms/molecule

^b This point is suspect due to a possible temperature error during the reaction.

TABLE 3

RECOVERED YIELDS OF TETRALIN, 1-METHYLINDAN AND NAPHTHALENE
AND HYDROGEN UPTAKE PER CARBON IN COAL^a

Coal	Reaction Time, min	Tetralin	1-methyl- indan	Naph- thalene	H uptake, Atoms/ Carbon Atom of Coal ^b
Illinois No.6	2.5	89.7	0.2	10.1	0.12
	5.0	86.3	0.3	13.4	0.17
	35	63.0	2.4	34.6	0.43
	60	51.9	3.5	44.6	0.55
Kaiparowitz	2.5	90.6	0.2	9.2	0.12
	5.0	86.1	0.3	13.5	0.17
	10	79.9	0.2	19.9	0.26
	25	72.7	1.9	26.8	0.34
	60	62.5	2.9	34.6	0.44

^a Yields of tetralin, 1-methylindan and naphthalene are normalized to 100%

^b Uses the yield of naphthalene recovered to estimate hydrogen uptake, neglects naphthalene and tetralin bound to coal products (~ 3%).

AN ISOTOPIC INVESTIGATION OF THE CHEMISTRY OF COAL HYDROLIQUEFACTION

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I. INTRODUCTION

We reported earlier on a deuterium tracer method for investigating the mechanisms of coal liquefaction.⁽¹⁻³⁾ The research involved the use of deuterium gas,⁽¹⁾ or deuterium gas and tetralin-d₁₂^(2,3) for hydrogenation, and the use of the deuterium as an isotopic tracer to follow the incorporation of hydrogen into the coal. After separation of the liquefaction products, the product fractions were analyzed for deuterium incorporation into different structural positions. It was found that when deuterium alone was used (without donor solvent) for liquefaction, the deuterium content of the products increased in the following order: oil < asphaltene < preasphaltene < residue. When deuterium and tetralin-d₁₂ were used, the deuterium contents of the product fractions were about the same. In both types of experiments, preferential incorporation of deuterium was found in the benzylic structural positions of each fraction. Similarly, preferential incorporation of protium was observed in the benzylic position of the recovered tetralin-d₁₂.

A number of related investigations have been reported on the use of deuterium as a tracer in coal hydrogenation research. Schweighardt, et al.⁽⁴⁾ examined a centrifuged liquid product from a Synthoil run after heating it to 450°C with deuterium gas; Kershaw and Barrass⁽⁵⁾ reported on the examination of products from the reaction of coal with deuterium gas using SnCl₂ as catalyst; Franz⁽⁶⁾ investigated the products from the reaction of a subbituminous coal with tetralin-1,1-d₂ at 427°C and 500°C; Cronauer, et al.⁽⁷⁾ reported on the interaction of deuterium-labeled tetralin with coal model compounds; King and Stock⁽⁸⁾ investigated the influence of coal and coal-related compounds on the exchange reaction between diphenylmethane and perdeuteriotetralin.

This paper presents the results of experiments which were conducted to investigate the respective roles of gas-phase and donor-solvent hydrogen in coal hydroliquefaction. Coal hydrogenation experiments were carried out with ²H₂/tetralin-h₁₂ and ¹H₂/tetralin-d₁₂ mixtures and tetralin-d₁₂ under N₂ pressure to study the mechanisms that are in operation.

II. EXPERIMENTAL

A. MATERIALS

A high-volatile A bituminous coal (80.1% C, 5.1% H, 1.6% N, 3.6% S, 9.6% O, by weight, daf basis, 7.7% ash) from the Loveridge Mine, Pittsburgh Seam was used. The coal was stored under nitrogen, ground to -200 mesh, and dried in vacuo for 4 hr at 115°C before use in each experiment. Technical-grade deuterium (>98 atom % deuterium, typical HD:0.5%) and high-purity nitrogen were utilized. Some of the tetralin-d₁₂ was prepared in our laboratories⁽³⁾, and some was purchased from the Aldrich Chemical Co., Inc. The isotopic purity of both materials was >99 atom % deuterium. The isotopic purity of tetralin-d₁₂ was determined by proton-NMR using p-dioxane as an internal reference.

B. EXPERIMENTAL AND ANALYTICAL PROCEDURES

A schematic outline of the experimental and analytical procedures is shown in Figure 1. Batch experiments were performed using a 1-liter stirred Autoclave Engineer's autoclave equipped with a coal injection system. In a typical experiment, the autoclave was charged with 25 g of tetralin, heated, and 25 g of coal was injected at temperature with the appropriate cover gas. After the scheduled reaction time had elapsed, the furnace was lowered from the autoclave, and the external surface was air-cooled. Also, water was circulated through the autoclave's internal cooling coils. After the autoclave had cooled to ambient temperature, the gas volume was measured using a wet test meter, and product gas samples were analyzed by GC-MS. The solvent was distilled from the product mixture and analyzed by NMR and GC-MS. The solid and liquid products were solvent fractionated into oil (hexane soluble, benzene soluble), asphaltene (hexane insoluble, benzene soluble), preasphaltene (THF soluble, benzene insoluble), and residue (THF insoluble) fractions. A portion of each fraction was combusted and its protium/deuterium ratio was determined by MS analysis of the resulting water. Each fraction was analyzed to determine its elemental composition. The fractions also were analyzed by proton and deuteron NMR spectrometry.

Proton NMR and deuteron NMR, spectra of soluble fractions, and recovered solvent mixtures were obtained by using a JEOL FX60Q FT NMR spectrometer. A flip angle of 45° was used which corresponds to $14\ \mu\text{s}$ for ^1H and $75\ \mu\text{s}$ for ^2H . The pulse repetition times were 6.0 and 9.0 s, respectively. Chloroform- d was used as the ^1H NMR solvent, and chloroform was used as the ^2H NMR solvent. Integrations were obtained using software supplied by JEOL, Inc. The GC-MS analyses were conducted by Shrader Analytical Laboratories, Inc., using a Pye-Unicam Model 105 chromatograph interfaced to an AEI Model MS-30 mass spectrometer.

III. RESULTS AND DISCUSSION

Three experiments were conducted to explore the roles of gas-phase and donor-solvent hydrogen on coal liquefaction. Tetralin- h_{12} , tetralin- d_{12} under $^2\text{H}_2$ or $^1\text{H}_2$, or N_2 pressure were used, as shown in the experimental matrix (Table 1). In each experiment, there was only one source of deuterium atoms: deuterium gas in Experiment 120 and tetralin- d_{12} in Experiments 121 and 122. In Experiment 122, nitrogen cover gas was used to eliminate those reaction pathways which involve gas-phase hydrogen.

TABLE 1
EXPERIMENTAL MATRIX FOR DONOR SOLVENT HYDROGENATION EXPERIMENTS

Experiment*	Coal +				
	Gas			Solvent	
	Protium	Deuterium	Nitrogen	Tetralin- h_{12}	Tetralin- d_{12}
D/P		X		X	
P/D	X				X
N/D			X		X

*Experiment name indicates gas isotopic composition/solvent isotopic composition (i.e., D/P refers to deuterium gas/tetralin- h_{12}).

A. PRODUCT YIELDS AND COMPOSITIONS

The product yields are shown in Table 2. It should be noted that the asphaltene and preasphaltene yields are lower than would be expected at 425°C and 15 MPa, particularly for the experiment in which nitrogen was the cover gas. We believe that this resulted from using unfavorably small amounts of reactants for the 1-liter autoclave to minimize the use of expensive tetralin-d₁₂. Nevertheless, previous coal hydrogenation experiments⁽²⁾ conducted with deuterium gas and tetralin-d₁₂ in a 1-liter and in a 250-ml autoclave showed that while higher soluble product yields were obtained in the smaller autoclave, the isotopic incorporation patterns were similar in both experiments.

TABLE 2
PRODUCT YIELDS FROM DONOR SOLVENT
HYDROGENATION EXPERIMENTS
(wt %)

Product	Experiment		
	D/P	P/D	N/D
Gas	10	11	9
Oil	24	19	16
Asphaltenes	8	4	1
Preasphaltenes	7	3	3
Residue	51	63	71

The deuterium contents of the product fractions are shown in Table 3. The deuterium content of the heavier fractions (asphaltenes, preasphaltenes, and residue) depend principally on the isotopic composition of the gas phase. These fractions have high atom % deuterium content in Experiment D/P, where ²H₂ gas and tetralin-h₁₂ were used, and low atom % deuterium content in Experiment P/D, where ¹H₂ gas and tetralin-d₁₂ were used. The atom % deuterium content of the heavy fractions is between these two extreme values in Experiment N/D where tetralin-d₁₂ was used under N₂ pressure. This indicates that the use of the inert gas, which precludes reactions with molecular hydrogen, allows pathways which are otherwise less significant to become more important in the reaction sequence. No obvious trend regarding the deuterium content was observed for the gas and oil fractions.

B. PRODUCT GAS COMPOSITIONS

The gas compositions, determined by gas chromatographic analysis, are shown in Table 4. The isotopic compositions of the product gases were determined by GC-MS analysis. The isotopic compositions of methane, ethane, and propane are shown in Table 5. The main results are summarized below:

- 1) The concentrations of the D₀ species can be correlated with the deuterium source used in the experiment. The D₀ species can form from the corresponding radicals by protium abstraction from the coal in any experiment, from the protium gas (Run P/D), or from tetralin-h₁₂ (Run D/P). The amount of D₀ species is reduced if the same radicals abstract deuterium from the tetralin-d₁₂ (Runs P/D and N/D) or ²H₂ gas (Run D/P). It appears that ²H₂ gas reacts more

TABLE 3
DEUTERIUM CONTENTS OF PRODUCTS
(Atom % of Total Hydrogen)

Product	Experiment		
	D/P	P/D	N/D
Gas	29	33	29
Oil	26	26	12
Asphaltenes	42	21	31
Preasphaltenes	34	15	28
Residue	<u>46</u>	<u>20</u>	<u>36</u>
Total Product	32	27	28

TABLE 4
PRODUCT GAS COMPOSITIONS
(Weight in Grams*)

Component	Experiment		
	D/P	P/D	N/D
CH ₄	1.10	1.36	0.94
C ₂ H ₄	0.01	0.01	0.01
C ₂ H ₆	0.58	0.63	0.43
C ₃ H ₆	0.01	0.01	0.01
C ₃ H ₈	0.35	0.35	0.24
i-C ₄ H ₁₀	0.01	0.03	0.05
n-C ₄ H ₁₀	0.08	0.10	0.08
i-C ₅ H ₁₂	0.02	0.01	-
n-C ₅ H ₁₂	0.02	0.02	0.02
CO	0.09	0.09	0.05
CO ₂	0.10	0.10	0.22
H ₂ S	<u>0.01</u>	<u>0.08</u>	<u>0.07</u>
Total	2.38	2.79	2.12

*Weights calculated on an all-protium basis

TABLE 5
ISOTOPIC COMPOSITIONS OF THE PRODUCT GASES
(%)

Component (Experiment)	D ₀	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆	D ₇	D ₈
<u>CH₄</u>									
D/P	28	29	30	13	0	-	-	-	-
P/D	36	25	13	14	12	-	-	-	-
N/D	40	24	14	11	11	-	-	-	-
<u>C₂H₆</u>									
D/P	8	31	32	19	10	0	0	-	-
P/D	23	17	19	15	10	10	6	-	-
N/D	*	*	*	11	9	12	13	-	-
<u>C₃H₈</u>									
D/P	27	24	17	10	10	6	4	2	0
P/D	35	31	16	7	3	2	3	2	1
N/D	36	27	14	9	3	4	5	2	2

*Interference from other species causes uncertainty in these values.

effectively with the radicals than tetralin-d₁₂ does.* This tentative conclusion is supported by previous experimental data⁽³⁾ obtained on the hydrogenation of coal with deuterium gas at 380°C without added donor solvent. The D₀ components in that experiment were for CH₄:3%, for C₂H₆:0%, and for C₃H₈:12%, which shows that the ²H₂ gas is a more effective deuterium source for the conversion of methyl, ethyl, and propyl radicals to the corresponding deuterated hydrocarbons than is tetralin-d₁₂. Hydrogen exchange with the solvent probably contributes to a lesser extent to the formation of these species, because even by the end of the experiment no more than one-third of the solvent hydrogen in any position has been exchanged. This may be due to the greater access of the hydrogen gas molecules to the pore structure of the coal compared with that of the solvent molecules.

- 2) Only minor differences were observed between the isotopic compositions of the gas products of the tetralin-d₁₂ run made with N₂ cover gas in one case (Run N/D) and under ¹H₂ pressure in the other (Run P/D). These results show that very little isotopic exchange takes place in the gas phase between hydrogen and hydrocarbons.
- 3) Fully deuterated methane and ethane were detected only in those experiments in which tetralin-d₁₂ was used. No such species were found in Experiment D/P, where tetralin-h₁₂ was used, and the deuterium source was ²H₂. This indicates that the CD₄ and C₂D₆ species were formed from the tetralin-d₁₂ only. It also appears that at least some of the CD₄ and C₂D₆ were formed from the solvent prior to the injection of the coal. Additional investigations are in progress to clarify this point.

*Alternately, isotopic exchange reactions may occur with the radical precursors.

C. COMPOSITION OF THE RECOVERED SOLVENT

1. GC-MS Analyses

The GC-MS analyses of the recovered solvents are shown in Table 6. In Experiment D/P, tetralin- h_{12} was used and the source of deuterium was 2H_2 gas. The isotopic distributions in the recovered tetralin and naphthalene are very similar. In both compounds, D_1 and D_2 species predominate, but sizable concentrations of D_3 and D_4 species are also present. The predominance of the D_1 and D_2 species, coupled with information from the NMR analysis of the solvent (Table 7), which show that 76% of the incorporated deuterium is in the α -aliphatic position, indicates that the α -tetralinyl radical has a significant role in the transfer of deuterium from the gas phase into the coal.

TABLE 6
ISOTOPIC DISTRIBUTIONS IN TETRALIN AND NAPHTHALENE
IN THE RECOVERED SOLVENTS
(%)

Component (Experiment)	D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}	D_{11}	D_{12}
<u>Tetralin</u>													
D/P	28	32	22	11	5	1	1	0	0	0	0	0	0
P/D	1	1	3	3	4	3	3	4	6	11	21	23	17
N/D	1	1	2	3	3	2	3	1	4	9	23	30	18
<u>Naphthalene</u>													
D/P	30	32	21	10	4	2	1	0	0	-	-	-	-
P/D	4	6	7	11	14	20	18	13	7	-	-	-	-
N/D	1	2	4	7	11	17	21	22	15	-	-	-	-

TABLE 7
ISOTOPIC COMPOSITION OF THE RECOVERED TETRALIN

Experiment	Incorporated Isotope	Atom % Isotope	Isotope Distribution (%)		
			H_{ar}	H_{α}	H_{β}
D/P	2H	13.5	10	76	14
P/D	1H	23.4	8	75	17
N/D	1H	18.6	9	74	17

The data from Experiment D/P also indicate that there is direct incorporation of deuterium gas into the coal. At the end of Experiment D/P there was only 13.5% deuterium in the tetralin. The α -aliphatic position of tetralin contained 31% deuterium ($13.5 \times 0.76 \times 3$) at the end of the experiment. Nevertheless, some of the coal products (asphaltene, preasphaltene, and residue), which formed throughout

the duration of the reaction, contained considerably more deuterium. This large amount of deuterium incorporation into the coal products strongly indicates that there is also a direct route for deuterium incorporation into the coal without the participation of tetralin.

In Experiments P/D and N/D, tetralin- d_{12} was used. The following observations can be made regarding these experiments:

- 1) In these experiments, the D_{11} and D_{10} (that is, H_1 and H_2) species predominate in the recovered tetralin. This is similar to Experiment D/P, in which the D_1 and D_2 species predominate. The predominance of the D_{11} and D_{10} species, together with the NMR analysis of the solvent indicating that 74-75% of the incorporated protium is in the α -position (Table 7), indicates that the α -tetralinyl radical has an important role in the hydrogen transfer. This is true for hydrogen transfer from the gas phase into the coal (Experiment P/D) as well as for hydrogen transfer from one site in the coal structure to another (Experiment N/D).
- 2) In contrast to Experiment D/P, where no species containing more than six deuterium atoms were detected, species with fully exchanged hydrogen (D_0) were found in each experiment. The extent of isotopic exchange was greater in these experiments because in contrast to Experiment D/P, isotopic exchange between the coal and the donor solvent could take place.
- 3) There is only a small difference between the isotopic distribution of the recovered tetralin obtained in Run P/D on the one hand, and Run N/D on the other. This indicates that the extent of isotopic exchange between the coal and the solvent is greater than it is between the hydrogen gas and the solvent. This same result is further substantiated by the data shown in Table 7.
- 4) The isotopic distribution found in the naphthalene is similar to that observed in the tetralin in Experiment N/D in that the least exchanged species (D_4 - D_8) are predominant. The isotopic distribution of the recovered naphthalene from Experiment P/D shows relatively large values for each of the species of low deuteration (D_0 through D_4), which indicates that a significant amount of the gas-phase protium exchanged with the naphthalene.

2. NMR Analyses

The recovered solvents were analyzed by proton and deuterium NMR spectroscopy. As an example, the deuterium NMR spectrum of the recovered solvent from Experiment D/P is shown in Figure 2. The tetralin α -aliphatic and β -aliphatic absorptions are shown at 1.8 ppm and 2.8 ppm, and the aromatic absorption of tetralin at 7.1 ppm. The aromatic absorptions at 7.4 and 7.8 ppm correspond to the β - and α -positions in naphthalene. There are additional absorptions in the spectrum (at 0.9, 1.3, 2.3, and 6.9 ppm) corresponding to deuterated alkylbenzenes, indan, methylindan, and cis- and trans-decalins, which form in small amounts during the reactions.

The isotopic composition data of the recovered tetralin, as determined by NMR analysis, are shown in Table 7. In Experiment D/P where tetralin- d_{12} and deuterium gas were used, 13.5 atom % deuterium was found in the recovered tetralin. In the other experiments, where fully deuterated tetralin was used, the protium incorporation ranged from 18.6% to 23.4%. The amount was larger in the tetralin from the experiment with the protium atmosphere (P/D) than from the experiment with the nitrogen atmosphere (N/D)--23.4 versus 18.6 atom % 1H .

The distribution of the incorporated isotope among the three structurally different sites in the solvent was nearly identical in each experiment. Approximately 75% was incorporated in the α -aliphatic position, 16% in the β -aliphatic, and 9% in the aromatic position. These proportions did not change significantly regardless of whether the reaction was conducted under protium or nitrogen pressure. The N/D system was also tested using reaction times of 1/4 and 1/2 hour. It was found⁽⁹⁾ that the extent of isotopic exchange with the solvent increases with time; however, the ratio of exchanged hydrogen in the three different structural positions of the solvent remains constant within this reaction time range (1/4 to 1 hour).

The following conclusions have been drawn from these measurements: (1) the relative reactivities of the α -aliphatic, β -aliphatic, and aromatic C-H bonds of tetralin at 425°C for ^1H - ^2H isotopic exchange between tetralin and coal are: 75:16:9; (2) these ratios do not change significantly regardless of whether N_2 or $^1\text{H}_2$ cover gas or whether tetralin- d_{12} / $^1\text{H}_2$ or tetralin- h_{12} / $^2\text{H}_2$ reactant combinations are used.

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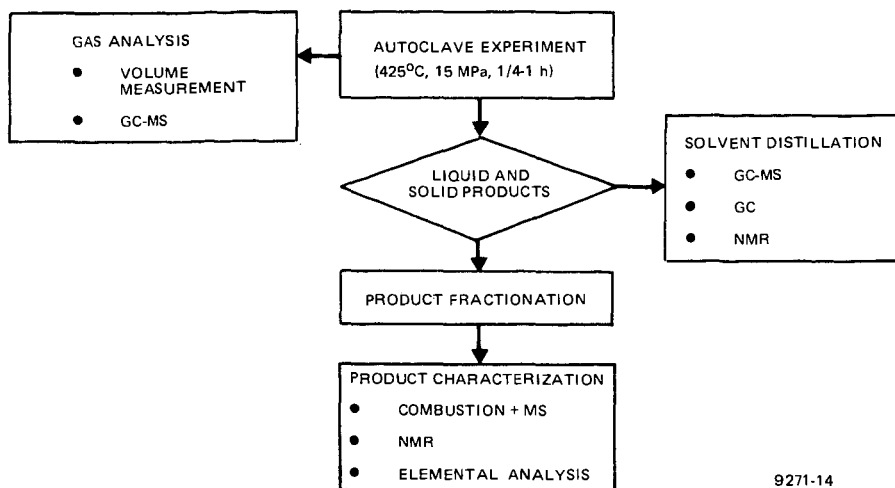


Figure 1. Experimental Procedure

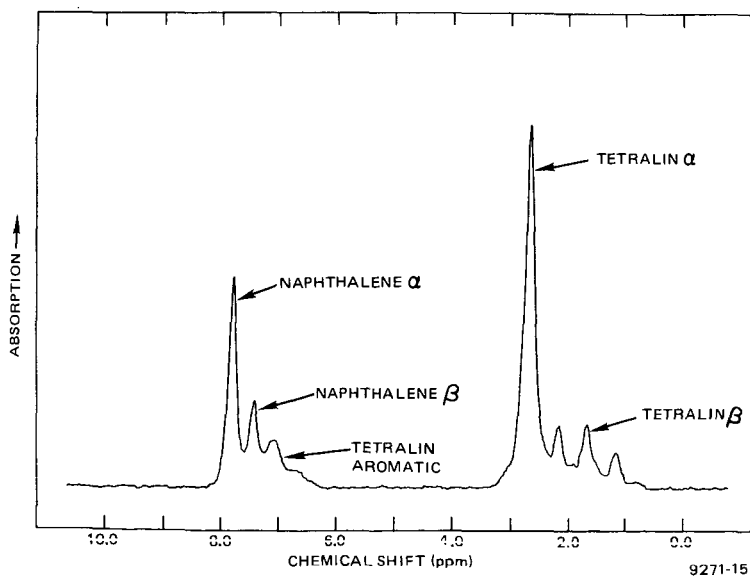


Figure 2. Deuteron NMR Spectrum of Recovered Solvent from Experiment D/P

MODEL PATHWAYS FOR HYDROGEN TRANSFER IN COAL LIQUEFACTION

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Hydrogen transfer from donor solvents to coal during liquefaction has been modelled by reactions between selected pure substrates. Model donors used were tetralin (control), Δ^1 - and Δ^2 -dialins, cyclohexanol and o-cyclohexylphenol, while anthracene and phenanthrene served as model acceptors. Experiments over the temperature range 250-450 C, at times from 0.1-10.0 hr, and donor/acceptor ratios of 0.12-16, revealed that, in general, three types of reactions occurred. In order of importance these were: (R1), the desired hydrogen transfer from donor to acceptor, (R2), the reversion of hydrogenated acceptor to original acceptor, either by elimination of molecular hydrogen or by disproportionation, and (R3), donor decomposition. Kinetic data showed that for every donor-acceptor pair (R1) was bimolecular, being of order one in each substrate. Also, Arrhenius parameters in all cases yielded activation entropies $\Delta S^\ddagger \sim -30$ eu, indicative of a tight transition state. These accord with our earlier suggestion that the mechanism of hydrogen transfer might involve concerted pericyclic group-transfer reactions that are thermally-allowed by the Woodward-Hoffmann rules for orbital symmetry conservation. Detailed kinetic data were also obtained for each of (R2) and (R3), permitting fairly complete description of the present model pathways for hydrogen transfer.

PARTICIPATION OF HYDROGEN IN THE HYDROGENOLYSIS AND HYDROGENATION
OF COAL-RELATED MODEL COMPOUNDS CATALYZED BY ZINC HALIDES

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INTRODUCTION

Model compound studies have recently been performed to help elucidate the types of reactions which occur during the liquefaction of coal in presence of ZnCl_2 (1-5). These investigations have shown that ZnCl_2 will catalyze the cleavage of ether, sulfide, and aliphatic bridges between aromatic centers and the hydrogenation of fused ring aromatics. It has also been demonstrated that the reactivity of a given structure can be strongly affected by the composition of substituents present on the aromatic nuclei. The purposes of the present work were to identify the role of molecular hydrogen in the hydrogenolysis and hydrogenation of coal-related model compounds and to demonstrate the differences in the ability of ZnCl_2 , ZnBr_2 , and ZnI_2 to activate H_2 .

EXPERIMENTAL

Apparatus

Reactions were carried out in a 300-cm³ stirred, stainless-steel autoclave fitted with a glass liner to facilitate introduction of reactants and removal of products. The pressure and temperature within the autoclave were monitored continuously. For most of the experiments described in this paper, the solvent and catalyst were preheated to reaction temperature within the autoclave. The reactant, dissolved in a small amount of solvent, was then injected into the autoclave from a small pressure vessel. Samples of the liquid products were withdrawn at prescribed times during the course of a run.

Materials

Model compounds were obtained commercially. These materials were dried but not purified before use. Benzene and cyclohexane, used as solvents, were dried by refluxing over a sodium-benzophenone mixture and then distilled under dry N_2 .

The ZnCl_2 , ZnBr_2 and ZnI_2 were dried in a vacuum oven overnight at 105°C and then stored in an N_2 -purged dry box. Weighing of the catalyst and transfer into the glass liner was also carried out in the dry box.

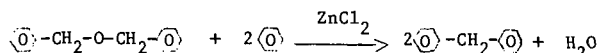
Product Analysis

The liquid products were analyzed by gas chromatography. Product identification was established by gas chromatography/mass spectrometry.

RESULTS AND DISCUSSION

Cleavage of Ether Linkages

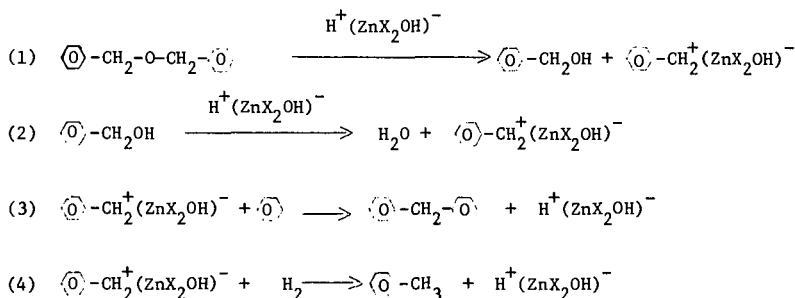
The effects of hydrogen partial pressure and catalyst composition on the hydrogenolysis of dibenzyl ether in benzene solution are listed in Table I. It is observed that in the presence of ZnCl_2 , diphenyl methane is the principal product formed and that the extent of reaction is unaffected by the presence or absence of molecular hydrogen. These results indicate that the overall reaction can be written as follows:



and that the hydrogen required for the formation of water derives from the benzene. As a result, molecular hydrogen does not appear to be essential for the progress of the reaction.

Table I shows that the catalytic activity of zinc halides decreases in the order $\text{ZnCl}_2 > \text{ZnBr}_2 > \text{ZnI}_2$. It is also seen that in the presence of ZnBr_2 and ZnI_2 , toluene is produced in addition to diphenyl methane. Moreover, while the extent of dibenzyl ether conversion is unaffected by the partial pressure of H_2 , the selectivity to toluene increases in direct proportion to the H_2 partial pressure. These results suggest that ZnBr_2 and in particular ZnI_2 are more effective in activating H_2 than ZnCl_2 but that even in an activated state hydrogen does not affect the rate of consumption of dibenzyl ether. However, once activated hydrogen becomes effective in the formation of toluene.

The accumulated evidence suggests that the hydrogenolysis of dibenzyl ether may proceed via the following sequence of steps

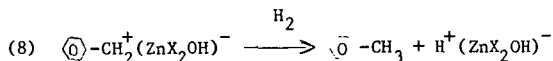
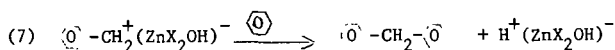
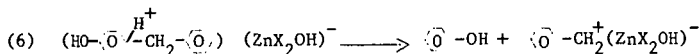
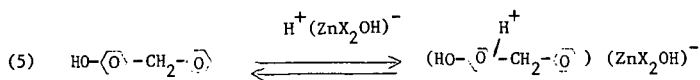


Studies in which the ratio of H_2O to ZnX_2 were varied clearly demonstrate that the active form of the catalyst is a Brönsted acid, $\text{H}^+(\text{ZnX}_2\text{OH})^-$. Cleavage of the ether is initiated by protonation of the ether and the rate of this reaction is affected by the composition of the zinc halide. The nature of the final reaction products is dictated by reactions 3 and 4 and the ratio of the rate coefficients associated with these reactions is determined by the catalyst composition.

Cleavage of Aliphatic Linkages

The hydrogenolysis of 4- hydroxydiphenyl methane (4HDM) and 1- benzyl- naphthalene (1BN) in benzene solution were studied to establish the effects of hydrogen partial pressure and catalyst composition on the cleavage of aliphatic linkages between aromatic nuclei. In the presence of zinc halide catalyst, 4HDM reacts to form phenol, diphenyl methane, and toluene. As shown in Table II, the hydrogen partial pressure has no effect on the conversion of 4HDM but the selectivity to toluene increases with the hydrogen partial pressure. The catalytic activity in this instance decreases in the order $\text{ZnBr}_2 > \text{ZnCl}_2 > \text{ZnI}_2$ and the selectivity to toluene increases in the order $\text{ZnBr}_2 > \text{ZnCl}_2 > \text{ZnI}_2$. The reaction of 1BN produces naphthalene, diphenyl methane and toluene. The effects of hydrogen partial pressure and catalyst composition on the reactions of this compound are similar to those for 4HDM.

The reaction products obtained from 4HDM and 1BN and the kinetics by which these reactants are converted to products (2) can be explained on the basis of the following mechanism:

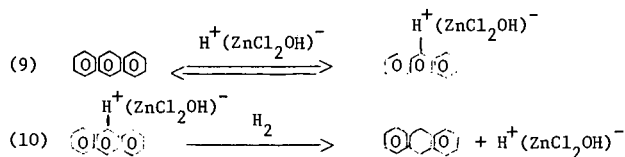


As in the case of the cleavage of ether linkages, reaction is initiated by protonation of the reactant. The primary difference is that this step is reversible and cleavage of the aliphatic linkages occurs in a subsequent rate limiting 1 step. The distribution of final products is governed by reactions 7 and 8.

Hydrogenation of Condensed Aromatics

Studies of the hydrogenation of fused-ring aromatics catalyzed by ZnCl_2 have shown (5) that 1-naphthol and anthracene undergo extensive reaction. The influence of hydrogen partial pressure on the extent of reaction and the distribution of products formed is shown in Table III. It is apparent that in the absence of hydrogen both reactants are converted extensively to tar via Scholl condensation. In the presence of hydrogen, 1-naphthol is hydrogenated to 1,2,3,4-tetrahydro-1-naphthol which then undergoes dehydration to form dihydronaphthalene. The latter compound is very reactive (5), undergoing hydrogenation to form tetralin and dehydrogenation to form naphthalene. The hydrogenation of anthracene produces primarily dihydroanthracene and smaller amounts of tetrahydroanthracene and octahydroanthracene.

The hydrogenation of both reactants is believed to proceed by sequential protonation and hydride addition, as exemplified by the first stages of anthracene hydrogenation shown below.



The formation of tetrahydro- and octahydroanthracene is assumed to involve a repetition of steps similar to reactions 9 and 10.

CONCLUSIONS

The following conclusions may be drawn from the present study:

- Zinc halide catalysts are active in their Bronsted acid form, e.g., $\text{H}^+(\text{ZnX}_2\text{OH})^-$.
- Cleavage of ether and aliphatic linkages between aromatic nuclei is indicated by protonation of the substrate and is unaffected by the presence of molecular hydrogen.
- Hydrogen transfer to benzylic groups liberated by the cleavage of dibenzyl ether, 4HDM and LBN and the selectivity for forming toluene from these reactants depends on the nature of the halide used.
- The hydrogenation of fused-ring aromatics involves molecular hydrogen and appears to proceed via sequential protonation and hydride transfer.

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ACKNOWLEDGMENT

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy.

Table I. Effects of H_2 Pressure and Catalyst Composition on the Reaction of Dibenzyl Ether

Catalyst	H_2 Press. (atm) ^a	Ether Conversion (%) ^b	Toluene	Product Yield ^c (%) Diphenyl Methane	Other
ZnCl ₂	35(N ₂)	81.3	0	88.0	10.2
ZnCl ₂	34	84.5	0	88.4	12.7
ZnCl ₂	82	79.0	0	88.4	9.1
ZnBr ₂	34	22.2	1.8	55.5	45.0
ZnI ₂	31	12.0	9.2	45.6	61.0
ZnI ₂	82	6.0	30.2	31.3	42.2

Reaction conditions: T = 225°C; Benzene = 80 cm³; Dibenzyl Ether ZnX₂ = 4.0 mole/mole.

^aAt reaction temperature.

^bFollowing 30 min of reaction.

^cBased on moles of dibenzyl ether reacted

^dBenzyl alcohol, benzyl halide and dibenzyl benzenes.

Table II. Effects of H_2 Pressure and Catalyst Composition on the Reactions of 4HDM and 1BN

Reactant	Catalyst	H_2 Press. (atm) ^a	Reactant Conversion (%) ^b	Toluene	Product Yield ^c (%) Diphenyl methane
4HDM	ZnCl ₂	37	27.1	5.4	38.2
4HDM	ZnCl ₂	71	27.9	10.5	30.0
4HDM	ZnBr ₂	44	62.2	3.4	42.0
4HDM	ZnI ₂	37	12.6	27.9	20.2
4HDM	ZnI ₂	68	13.7	49.9	13.7
1BN	ZnCl ₂	44	16.8	12.9	35.2
1BN	ZnCl ₂	68	17.4	20.3	31.7
1BN	ZnBr ₂	81	22.7	6.9	51.8
1BN	ZnI ₂	51	13.4	37.3	26.7

Reaction conditions: T = 325°C; Benzene = 80 cm³; 4HDM/ZnX₂ = 40 mole/mole; 1BN/ZnX₂ = 1.0 mole/mole

^aAt reaction temperature.

^bFollowing 2 hr of reaction.

^cBased on moles of dibenzyl ether reacted.

Table III. Effects of Gas Composition on the Reactions of 1-Naphthol and Anthracene

Products from 1 - Naphthol	H ₂ Conversion ^a (%)	N ₂ Conversion ^a (%)
alkylbenzenes	0.1	-
tetralin	14.0	0.1
dihydronaphthalene	2.1	0.2
naphthalene	3.4	1.6
1-tetralene	3.5	1.6
1,2,3,4 -tetrahydro-1-naphthol	0.1	trace
5,6,7,8 -tetrahydro-1-naphthol	2.1	trace
2-naphthol	-	0.5
tar	-	77.0
Products from Anthracene	H ₂ Conversion ^a (%)	N ₂ Conversion ^a (%)
alkylnaphthalenes	0.4	-
octahydroanthracene	3.2	-
tetrahydroanthracene	13.0	trace
dihydroanthracene	51.0	0.9
tar	-	94.0

Reaction conditions: T = 325°C; P = 107 atm; Cyclohexane = 50 cm³; 1 - naphthol / ZnCl₂ = 1.85 mole/mole
Anthracene/ZnCl₂ = 1.85 mole/mole

^a Following 1 hr of reaction.

HYDROGENOLYSIS OF DILUTE SOLUTIONS OF DIBENZYL IN TOLUENE AT COAL LIQUEFACTION CONDITIONS. Lonnie W. Vernon, Exxon Research and Engineering Company, P. O. Box 4255, Baytown, Texas 77520, and Ralph Livingston and Henry Zeldes, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

Previous pyrolysis studies (L. W. Vernon, Fuel 59 102 (1980)) have shown that the conversion of dibenzyl in the presence of both tetralin and molecular hydrogen or in the presence hydrogen alone proceeds along two parallel reaction paths. Toluene is produced by a thermolysis reaction in which the rate controlling step is the thermal cleavage of the β -bond in dibenzyl. Benzene and ethyl benzene are produced by a hydrogenolysis reaction. The hydrogenolysis reaction is thought to proceed via a hydrogen atom chain carrier. ESR studies (R. Livingston, H. Zeldes, and M. S. Conradi, J. Amer. Chem. Soc. 101 4312 (1979)) have shown that benzyl is the predominant radical in the system during the pyrolysis of dilute solutions of dibenzyl in toluene. In the present study dilute solutions of dibenzyl in toluene have been pyrolyzed at 450°C, contact times of 1-3 minutes, and hydrogen pressures of 0-15 MPa. Under these conditions the conversion of dibenzyl is low (about 2-7%). The major product is benzene and the concentration of benzene increases with increasing hydrogen pressure. These results are consistent with the proposed mechanism for the conversion of dibenzyl in the presence of molecular hydrogen. In the present study, the free radical reaction is initiated by the thermolysis of dibenzyl and the benzene is produced by the hydrogenolysis of toluene via a hydrogen atom carrier.

ESR STUDY OF BIBENZYL DURING PYROLYSIS WITH AND WITHOUT HYDROGEN. Ralph Livingston and Henry Zeldes, Chemistry Division, Oak Ridge National Laboratory,* Oak Ridge, Tennessee 37830 and Lonnie W. Vernon, Exxon Research and Engineering Company, P. O. Box 4255, Baytown, Texas 77520

Free radicals have been observed during pyrolysis of bibenzyl in solution and in an earlier report (R. Livingston, H. Zeldes, and M. S. Conradi, J. Amer. Chem. Soc. 101, 4312 (1979)) the equilibrium $C_6H_5CH_2CH_2C_6H_5 + C_6H_5CH_2 \rightleftharpoons C_6H_5CHCH_2C_6H_5 + C_6H_5CH_3$ was described. The fluid sample at high pressure is circulated through a heated quartz capillary located in the ESR cavity where the contact time at pyrolytic temperature is approximately 0.5 sec. Dilute bibenzyl in toluene gives a spectrum of predominantly $C_6H_5CH_2$, whereas in an inert solvent (benzene) $C_6H_5CHCH_2C_6H_5$ predominates. In the present study 0.1 to 1 M bibenzyl in toluene and in benzene have been studied from 507°C to 553°C at 1300 psi. The ESR spectra have been examined to verify radical content and samples have been collected after pyrolysis for GC. Where $C_6H_5CHCH_2C_6H_5$ predominates the usual distribution of products reported for bibenzyl (M. Poutsma, Fuel, 59, 335 (1980)) are seen with strong contributions from radical-radical coupling products. Where $C_6H_5CH_2$ predominates the product distribution alters greatly and the burnup of bibenzyl falls to 1/3 to 1/7 the value in benzene solution depending on concentration and temperature. High pressure hydrogen has been injected prior to pyrolysis and substantial increases in the yields of benzene and ethylbenzene have been observed. *Research at this laboratory was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy, under Contract W-7405-eng-26 with Union Carbide Corporation.

HYDROGEN-CARBON MONOXIDE REACTIONS IN LOW-RANK COAL LIQUEFACTION

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The primary role of the gas phase in low-rank coal liquefaction appears to be the stabilization of pyrolysis products from the coal via hydrogenation and, to a much lesser extent (in a non-catalytic system), hydrogenation of coal liquids. Hydrogen donor compounds and, to a lesser extent, the bulk of the solvent perform similar functions; that is to provide another source of hydrogen in addition to that in the gas phase to quench free radicals. Solvent effects will not be discussed in this paper. Carbon monoxide and water are the favored reactants over pure hydrogen at all temperatures from 350°C to 480°C for the liquefaction of low-rank coals. The amount of carbon monoxide consumed is dependent on the quantity of coal present, indicating that the driving force is the number of reactive sites initially present in the coal.

EXPERIMENTAL

Time Sampled Batch Autoclave

Studies on batch kinetics were carried out in a 1-liter, magnetically-stirred autoclave, which is outfitted to enable the charging of a slurry to the preheated reactor and for timed sampling of the gas and slurry phase during the course of an experiment. Hot charging brings the slurry to temperature in under 3 minutes, thereby eliminating the 1- to 2-hour heat-up associated with typical autoclave operation (1,2). Alternately, the slurry can be charged at an intermediate temperature and heated in stages to observe the effects of temperature change. An example of pressure, temperature, and gas composition data obtained where the autoclave was charged at room temperature and heated to reaction temperature is depicted in Figure 1. One thing to note is that the production of carbon dioxide and the consumption of carbon monoxide is kinetically rapid at temperatures above about 350°C. The experimental conditions for data reported in this paper are given in Table 1.

Coal

The coal utilized in the experiments was a lignite obtained from a mine located near Beulah, North Dakota (Sample B3). Proximate-ultimate data have been presented earlier (2). Lignite coals are very reactive and are reported to evolve carbon dioxide at temperatures as low as 200°C (3). Dried lignites readily react with air and can spontaneously combust. Coal samples are therefore stored wet under nitrogen in lump form and pulverized just prior to use.

The B3 lignite sample was pyrolyzed in a stream of inert gas at 500°C by Timpe (4) at GFETC under an Associated Western University grant. The sample produced 0.17, 2.05, 14.92, 1.50, and 0.67 wt pct (MAF coal) of H₂, CO, CO₂, CH₄, and C₂-C₄ hydrocarbon gases, respectively. These data are in agreement with previously reported distillation assay data (5). In batch autoclave tests, the total gas discharged at the end of a run is slightly increased over the amount charged due to CO₂ production. For a charge of 3 moles of gas and 50 gm of MAF coal, a CO₂ concentration of about 5 mole pct is typical.

TABLE 1
Experimental Conditions for Reported Studies

Figure-Curve	Run No.	Range of Temp. (°C)	Reactants Charged				Total H ₂ O (gm)
			CO ₂ (moles)	H ₂ (moles)	MAF Lignite (gm)	Solvent (gm)	
2,3	30	400-470	1.8	1.6	44	163	42
2,3	21	400-480	1.8	1.6	--	--	50
2,3	22	400-480	1.8	1.6	--	200	50
4-1	34	400-440	4.0	--	--	--	50
4-2	35	206-440	4.0	--	51	182	1
4-3	32	440	4.0	--	45	164	40
5-4	39-2	400-480	3.1	--	26	92	23
5-5	39-1	350-470	3.5	--	52	192	47
5-6	62	350-470	2.6	--	140	238	63

Lignitic coals also produce about 10 wt pct (MAF coal) of water during pyrolysis. This water was most probably bound as water of hydration (such as in clays or in humic acid structures) and would not be lost during drying at 110°C. This is potentially "inherent" water that could react with carbon monoxide via the shift reaction.

Solvent

The solvent used in the experiments was mainly a commercially obtained anthracene oil. In autoclave work the solvent was spiked with tetralin (about 7 wt pct of the slurry charged) to minimize coking during rapid heat-up. In the observed gas composition changes, the solvent primarily effects methane production (1). As will be discussed later, the solvent does not effect observed CO₂ or CO values and only slightly effects observed H₂ values.

Gas Analysis

Gas samples were analyzed by on-line GC, eliminating any air dilutions. The column used was a 12 to 14-ft, 1/4-inch 316 SS tube packed with Porapak QS. The GC was a Gow Mac maintained at 50°C employing argon as the carrier gas. Utilizing argon carrier gas results in high hydrogen sensitivity (0.02 mole pct), moderate sensitivity for CO₂ and CH₄ (0.1 to 0.3 mole pct), and poor sensitivity for propane (0.5 mole pct). Calibration gas and reactant gases were purchased pre-mixed from a local supplier.

The gas samples were removed from the gas phase of the autoclave. Previous data indicate that CO₂ and CH₄ are preferentially dissolved relative to H₂ and CO (1) in the liquid phase. Ratios of the mole pct of H₂, CO, CO₂, and CH₄ dissolved in the slurry to those in the gas phase were 0.87, 0.74, 1.38, and 1.10, respectively, at 435°C and 4500 psi. However, the value of dissolved gas was 37 ml (STP)/gm slurry; about 0.3 moles for a 200-gm charge, which was an order of magnitude less than in the gas phase, assuming all of the solvent was in the slurry phase. For the solvent in these tests, 40 to 60 pct was in the gas phase; therefore, there would be only about 0.1 to 0.2 moles of dissolved gas, which would have little effect on the composition of the analyzed gas phase. The moles of gas charged plus the moles of methane produced were found to be equal to the moles of gas metered from the autoclave at the end of an experiment plus the gas lost during sampling. Only special experiments enabled the observation of the direct production of CO₂ from lignite. In most cases the moles of CO charged equaled the moles of CO₂ and CO at the end of an experiment.

RESULTS

Experiments have been made to determine how CO and CO-hydrogen interact with the reactor walls, water, solvent, wet coal, and dry coal.

In Runs 21, 22, and 30, H₂-CO (50:50 wt pct) was reacted with water, water-solvent, and water-solvent-coal, respectively, in temperature-stepped experiments. The changes in the gas phase concentrations of CO and H₂ are depicted in Figures 2 and 3. For water and water-oil systems (Fig. 2), CO is slowly consumed only at temperatures above 400°C. Adding wet lignite dramatically increases the consumption of CO even at temperatures below 400°C. In the water-only experiments, the amount of CO consumed is the same as the amount of hydrogen produced. However, in water-oil and in water-oil-coal systems, a slight hydrogen decrease (note expanded scale) is observed (Fig. 3). In systems with oil or oil-coal present, some of the decrease is due to dilution (hydrocarbon gas production and/or the direct production of CO₂ from coal caused an increase of about 10 pct in the total gas in the reactor by the end of a run). As indicated by the data, slightly more H₂ appears to be consumed when coal is present in the oil. These data also illustrate that CO is preferentially reacted at all temperatures.

Figure 4 depicts data for reaction of CO with dry and wet coal-oil slurry. For comparison, data from Run 34 are shown where no coal or oil was present. Run 32 was a hot-charge experiment, which shows the rapid initial CO consumption when wet lignite is present. In Run 35, the lignite was dried in the solvent at 110°C with a nitrogen purge prior to charging. While Run 35 was a slow heat-up with temperature stepping (1 hr at 400°C and 1 hr at 440°C), CO consumption and CO₂ production were essentially complete when 400°C was reached, and very little hydrogen was produced.

The amount of CO consumed has also been found to be dependent on the amount of coal charged. Figure 5 depicts CO consumption when 26, 52, or 140 gms of MAF lignite were charged to the autoclave. For Run 62, where 140 gms were charged, over 95 pct of the CO charged was consumed. The shaded areas (the difference between the top and bottom lines) indicate the moles of H₂ observed versus time. When 140 gms of lignite was present, the amount of hydrogen observed was greatly reduced, indicating that a direct reaction with lignite to produce CO₂ is favored over reactions that would produce both CO₂ and H₂.

CONCLUSIONS

The data that have been presented support the following conclusions:

- a) The shift reaction

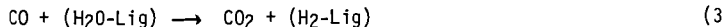


is not catalyzed by the reactor walls or an aromatic solvent (Figs. 2 and 4). However the solvent does undergo some slow hydrogenation (Fig. 3).

- b) The presence of lignite catalyzes the shift reaction, but a reaction such as



or



is favored, especially at lower temperatures (Figs. 1 and 5).

- c) The reported equilibrium values (6) for the shift reaction decrease with increasing temperature from 28.25 at 327°C to 6.3 at 527°C. In runs without lignite, the concentration of CO steadily decreases at all temperatures with time and is at all experimental times far from an equilibrium value. With coal present, the amount of CO consumed is directly dependent on the amount of coal charged. This indicates that the coal has a certain number of reactive sites and that when they have reacted, the reaction essentially stops. While the shift reaction is no doubt occurring, it does not appear to be the most important reaction, at least not in these experiments.
- d) H₂ is produced via the shift reaction (Fig. 5) in CO-H₂O systems. However, since its concentration does not increase when both H₂ and CO-H₂O reactants are present (Fig. 3), hydrogen must be reacting. However, the net consumption of charged hydrogen is small compared to that of CO. Therefore, in competitive reactions CO reacts more rapidly than hydrogen.

The preceding statements re-emphasize the fact that CO undergoes reactions with lignite that are kinetically more favorable than those with hydrogen, and that these reactions are favorable throughout the temperature range studied (350-480°C).

LITERATURE CITED

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